

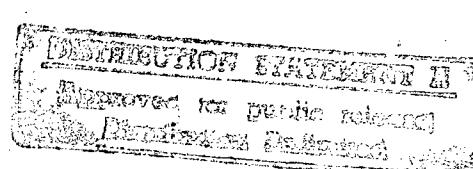
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# ***JPRS Report—***

# **Science & Technology**

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***Central Eurasia:  
Chemistry***



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# Science & Technology

## CENTRAL EURASIA: Chemistry

JPRS-UCH-93-002

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28 January 1993

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**Catalytic Properties of Alkaline Phosphatase, Immobilized on Modified Silica Gel Containing SH-Groups**

927M0229A Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA - SERIYA 2 KHIMIYA in Russian Vol 26 No 1, Jan-Feb 92 (manuscript received 19 Apr 91) pp 20-24

[Article by R. Khamvi, Ye. S. Chukhray, M. N. Veselova, T. M. Roshchina, and O. M. Poltorak, Chair of Physical Chemistry; UDC 577.156]

[Abstract] Alkaline phosphatase (KF 3.1.3.1) from chick intestine is unstable in adsorption layers on silica gel surfaces, but is yet stable enough to sustain catalytic reactions under heterogeneous conditions at alkaline pH values on a silica gel surface modified with cholesterol. This indicates the presence of large hydrophobic groups on the protein surface. By using a silica gel carrier modified with organic compounds containing SH-groups (LIK-21), it appears possible to prepare stable adsorption layers at alkaline pH values for use as effective heterogeneous biocatalysts. In the present work adsorption layers of alkaline phosphatase (3.1.3.1) on modified silica gel containing SH-groups (LIK-21) were prepared and it was demonstrated that these layers are very stable at pH 8.5 in tris-HCl buffer. During the immobilization process, inactive associates become aggregated resulting in the formation of an oligomerically uniform heterogeneous biocatalyst similar in catalytic properties to that of corresponding form of the enzyme in solution. Figures 3; references 4: 3 Russian, 1 Western.

**High Temperature Decomposition of Ozone with Monolithic Porous Catalysts Based on Nichrome and Various Additives**

927M0229B Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA - SERIYA 2 KHIMIYA in Russian Vol 26 No 1, Jan-Feb 92 (manuscript received 18 Apr 91) pp 29-33

[Article by L. I. Belskikh, L. Ye. Gorlenko, and G. I. Yemelyanova, Chair of Physical Chemistry; UDC 541.128]

[Abstract] High temperature decomposition of ozone in ozone-air mixtures at high throughput rates and high moisture content requires the use of effective catalysts having high heat resistance, gas permeability, and mechanical strength. Pelletized catalysts bearing an active phase are unsuitable for this purpose owing to attrition under hydraulic stress. Whole metal catalysts are currently known to exist which can provide large contact surfaces to the air and they are heat and wear resistant. Catalyst permeability becomes a major factor when treating large volumes of air. This factor also determines the hydraulic resistance value of the filter. In the present work a study was made of the catalytic activity and stability of monolithic porous catalysts based on stainless steel and nichrome powders. The catalysts were modified by oxidation and addition of structure-forming and promoter additives prior to compression. Tests showed that nichrome catalysts containing zirconium oxide additive are optimal. Figures 2; references 8: 6 Russian, 2 Western.

**Electrocatalytic Behavior of Sulfamic Acid on Platinum**

927M0229C Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA - SERIYA 2 KHIMIYA in Russian Vol 26 No 1, Jan-Feb 92 (manuscript received 19 Apr 91) pp 46-49

[Article by T. M. Grishina and O. K. Lebedeva, Chair of General Chemistry; UDC 541.183.03]

[Abstract] Sulfamic acid is used widely in many diverse branches of industry as an electrolyte in electroplating processes, as a catalyst in organic synthesis, to bleach hides, as a cleaning agent in nuclear reactors, etc. Increased industrial applications of this acid has necessitated the problem of separating it from waste effluents. In the present work a study was made of the adsorption of sulfamic acid under open circuit conditions at input potentials of 0.05, 0.5, and 1.2 volt on Pt/Pt by galvanostatic and potentiodynamic charge curves. It was demonstrated that the presence of sulfamic acid causes redistribution of adsorbed hydrogen among the energy bonds although its quantity changes little. Sulfamic acid to a large degree affects the sorption of oxygen, and there is a significant change in oxygen sorption at input potentials of 0.05 and 1.2 volt. This is evidently related to the ionic structure of the sulfamic acid molecule. Figures 3; references 4 (Russian).

**Study of Structure Formation in Low Molecular Dimethylsiloxane Raw Rubber with 'Unbalancing' Type Catalyst**

927M0230E Moscow PLASTICHESKIYE MASSY in Russian No 2, Feb 92 pp 38-39

[Article by D. V. Smelyanskiy, N. A. Glotova, N. P. Zakrasina, N. D. Fedyukin, and I. K. Kayurullin; UDC 678.842.044.028]

[Abstract] Two-component sealants and cold curing compounds based on low molecular weight siloxane rubbers are used throughout modern technology, especially construction. These substances cure in any thickness to form a grafted material that is resistant to weather. The silicon-organic compositions cure after mixing two components, one containing the rubber, grafting agent, filler, plasticizer, and other ingredients, and the other the catalyst. Preliminary research shows that the viscosity of the mixtures of the siloxane rubbers and certain organometallic compounds in the absence of traditional grafting components, such as tetraethoxysilane, increases. In the present work a study was made of the processes that take place in a rubber containing a tin-organic "unbalanced" catalyst and the corresponding increase in viscosity and gel formation after prolonged storage. Specifically, a low molecular weight dimethylsiloxane rubber of 28,600 mean molecular weight having terminal hydroxyl groups and 2.7 Pa-seconds viscosity was used with stannous dioctoate catalyst. Structure formation was observed by IR-spectra and viscosity changes recorded. It was demonstrated that it is possible for a complex to be formed between the  $\text{Sn}^{+2}$  ion and the polydimethylsiloxane-diol terminal OH-groups with subsequent polymerization of the rubber accompanied by a 5-fold increase in molecular weight after 5 months storage. Figures 2; references 6: 4 Russian, 2 Western.

### Palladium Catalyst Systems Applied Onto Ion Exchangers

937M0005A Moscow DOKLADY AKADEMII NAUK  
in Russian Vol 324 No 1, May 92 (manuscript received  
6 Feb 92) pp 124-127

[Article by A.K. Zharmagambetova, Ye.Ye. Yergozhin, academician of the Republic of Kazakhstan Academy of Sciences, R.K. Ashkeyeva, and A.Sh. Kuanyshov, Organic Catalysis and Electrochemistry Institute imeni D.V. Sokolskiy, Republic of Kazakhstan Academy of Sciences, Chemical Sciences Institute imeni A.B. Bekturova, Republic of Kazakhstan Academy of Sciences, and Kazakhstan State University imeni Al-Farabi, Alma-Ata; UDC 541.128+678.744]

[Abstract]  $\text{PdCl}_2$  was adsorbed on sorbents with dithiole groups based on cellulose and a copolymer of styrene with divinylbenzene so as to produce a catalyst with a palladium content of 5 wt.-%. The complexes were rinsed in water, air-dried, and studied to determine their effectiveness in the hydrogenation of successive portions of allyl alcohol on one weighted portion of catalyst. Chromatography studies established that propanol is the main hydrogenation product on a complex with a cellulose matrix and that as the catalyst is used repeatedly, the propanol yield increases and the yield of propionic aldehyde decreases. On the study palladium complex with a styrene-divinylbenzene copolymer, on the other hand, the process occurs primarily via isomerization, and when the catalyst is reused, the propionic aldehyde yield increases from 74 to 90%. The study catalyst also proved to have rather high stability: even after it was used five times, the rate at which allyl alcohol disappeared in the catalyst did not diminish. The studies thus established that the nature of the polymer substrate has an important effect on the properties of catalyst systems and that there is a definite dependence between the electron state of the palladium in catalyst systems and those systems' catalytic activity. Figures 2, table 1; references 7: 3 Russian, 4 Western.

### The Catalytic Synthesis of Organic Matter From $\text{CO}_2\text{-H}_2\text{O}$ and $\text{CO}_2\text{-H}_2\text{S}$ Initiated by Physical Heat

937M0008B Moscow DOKLADY AKADEMII NAUK  
in Russian Vol 323 No 2, Mar 92 (manuscript received  
4 Nov 91) pp 299-305

[Article by Ya.M. Paushkin, academician, Belarus Academy of Sciences, G.P. Lebedeva, A.B. Urin, and E.Kh. Kurashova, Mineral Fuels Institute, Moscow; UDC 662.743]

[Abstract] It was previously believed that the formation of simple and complex organic matter from  $\text{CO}_2$  and  $\text{H}_2\text{O}$  was only possible during photosynthesis in living nature. A number of researchers recently demonstrated that formaldehyde, formic acid, and other acids will form when solutions of  $\text{CO}_2$  in  $\text{H}_2\text{O}$  are irradiated with a strong (as strong as daylight) lamp, ultraviolet light, or a  $\gamma$ -source. In a continuation of this line of research, a series of experiments was conducted to determine the possibility of synthesizing organic matter from inorganic carbonates and water initiated by physical heat and catalysts at temperatures of 423-433 K (60 to 150°C) with the carbonates  $\text{CaCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ , and  $\text{K}_2\text{CO}_3$ . At temperatures up to 373

K, the experiments were conducted in an open system. Above 473 K they were conducted in an autoclave under a pressure of 0.6 to 0.8 MPa. The time of the experiments at the specified temperatures ranged from 10 to 45 hours. All of the starting substances and equipment were subjected to chromatographic analysis to ensure that they were free of extraneous organic impurities. In the absence of catalysts, no formation of organic matter from the carbonates and water was observed. Lower acids were observed to form in the presence of catalysts based on nickel, cobalt, copper, iron, and magnesium, however. The chromatograms recorded during most of the experiments conducted were different with respect to the position of their peaks. Overall, however, they indicated the formation of a complex mixture of high-boiling substances containing 20 to 40 or more carbon atoms. Thin-layer chromatographic analysis of several of the specimens confirmed the presence of aromatic compounds. Solid paraffins were identified in several experiments. Most of the organic matter produced contained about 55% C, 10% H, and 35% O. One specimen analyzed was found to consist of 85% C and 15% O, however. The experiments confirmed that in the presence of the appropriate catalysts and physical heat, carbonates and water could react in several different ways to yield oxygen-containing substances, aromatic compounds, unsaturated compounds, and saturated hydrocarbons. Figures 3, table 1; references 9: 8 Russian, 1 Western.

### The Catalytic Synthesis of Methyleneethyl Ethynylcarbinol-Based Pyridine Bases

937M0013A Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 1, Jan-Feb 92 (manuscript received 8 May 91) pp 41-44

[Article by M.F. Fauzullayeva, T.S. Sirlibayev, and A. Ikramov, Tashkent Red Labor Banner Order State University imeni V.I. Lenin; UDC 547(821+362+281)546.171.1]

[Abstract] The reaction of methyleneethyl ethynylcarbinol and acetic aldehyde with ammonia in the presence of a Zn-Cr-Al catalyst at temperatures of 300 to 440°C was studied. The methyleneethyl ethynylcarbinol was synthesized based on acetylene and methyl ethyl ketone by Favorskii's reaction. The experiments were conducted in a continuous, completely airtight system with a methyleneethyl ethynylcarbinol:acetic aldehyde:ammonia ratio of 1.0:1.1:3.0 and a reagent space velocity of 86.0 to 86.3/h. The reaction products were analyzed first by thin-layer chromatography and then by gas-liquid chromatography on an LKhM-80MD laboratory chromatograph. The best results were obtained at 440°C, at which point the following products were identified (wt.-%): 2-methylpyridine, 17.6; 4-methylpyridine, 15.9; 2,3,4-trimethylpyridine, 17.3; 2-methyl-6-ethylpyridine, 23.1; 2,3,6-trimethylpyridine, 15.1; and acetonitrile, 11.0. The following sequence of the formation of alkylpyridines from methyleneethyl ethynylcarbinol was proposed: At a high temperature over a Zn-Cr-Al catalyst, acetylene alcohol splits into starting methyl ethyl ketone and acetylene. In the presence of hydrating catalysts, the latter complexes with water and forms acetic aldehyde that is then transformed into crotonaldehyde (via crotonic condensation) that in turn reacts with the methyl ethyl ketone to form the main reaction product 2-methyl-6-ethylpyridine. This in turn triggers the formation of the remaining reaction products.

The correctness of this proposed reaction mechanism was verified by backward synthesis. Table 1; references 10: 9 Russian, 1 Western.

### Use of Catalysts in the Thermochemical Treatment of Metals and Alloys

937M0036A Moscow KHIMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE in Russian No 3, Mar 92 pp 24-25

[Article by Yu.A. Sobolev: "Use of Catalysts in the Thermochemical Treatment of Metals and Alloys"; UDC 621.785:66.0973]

[Abstract] Extensive use of thermochemical treatment is limited because of the length of the processes and the high temperatures required. The author substituted boron for sodium carbonate used for the acceleration of cementation in a carbonizer because boron has diffusion properties similar to those of carbon. Thermochemical treatment basically is conducted or accelerated by addition to the saturating medium of substances containing alkaline-earth metals or amines. According to the literature, practical data, and the results of work on boronizing, alkaline-earth metal compounds are decomposed on the substrate to produce the alkaline-earth atom, which, possessing the smallest ionization potential of all the elements, donates an electron to the substrate and forms a dipole with a positively charged top. An electron deficit is created in the surface layer, which antibonds the substrate lattice, ionizes the diffusion elements, and thus intensifies the thermal treatment. Ammonia may play the double role of saturating component and catalyst in nitrocementation. A search should be made for compounds having a larger dipole moment than alkaline-earth metals and  $\text{NH}_4^+$ . References: 4 Russian.

### Rate Constants of o-Phenylenediamine Complexes of Ni(II) Based on Polarographic Catalytic Current. Complex Formation With Acetate Anions

937M0045A St. Petersburg ZHURNAL OBSHCHEY KHIMII in Russian Nov 91 pp 2378-2388

[Article by Ya. I. Turyan; UDC 541.49.53.081:543.251]

[Abstract] This review of the literature on the limiting polarographic catalytic current in the reduction of nickel(II) ions in the system  $\text{Ni}^{2+}$ -o-phenylenediamine system determines the stability constants of o-phenylenediamine complexes of nickel(II). The systems  $\text{Ni}^{2+}$ -o-phenylenediamine ( $\text{NaClO}_4$ ) and  $\text{Ni}^{2+}$ -o-phenylenediamine in the presence of another acetate anion ligand are considered separately. The average stability constants of o-phenylenediamine (A) complexes of nickel obtained were: in 0.1 mol/l  $\text{NaClO}_4$   $\beta_1^A$ (7.8 q 1.5) y  $10^2$ , in 1.0 mol/l  $\text{KOA}$   $\beta_1^A$ (9.8 q 1.7) y  $10^1$ ,  $\beta_2^A$ (2.2 q 0.3) y  $10^6$ ,  $\beta_3^A$ (5.4 q 0.7) y  $10^8$ . With an electrically neutral ligand, the value of  $\beta_1^A$  varies little with ionic strength of the solution. Complexes of  $\text{Ni(A)}_2^{2+}$  and  $\text{Ni(A)}_3^{2+}$  were also

detected. These complexes may actually be mixed acetate-o-phenylenediamine complexes. Statements from earlier works that  $\text{Ni}^{2+}$  ions do not form a chelate structure with A make it difficult to understand the lack of correlation between  $K_a$  of the ligand and  $\beta_1^L(\text{Ni}^{2+})$  for Py and A. Reaction rate variations indicate specifics of complex formation with the amino group in the o position, increasing the stability of complexes in comparison to Py. Figures 4; References 44: 13 Russian, 31 Western.

### Catalytic Activity of Organophosphorus Acid Amides in Formation of Thiosemicarbazides

937M0045C St. Petersburg ZHURNAL OBSHCHEY KHIMII in Russian Nov 91 pp 2547-2552

[Article by N. I. Yanchuk; UDC 547.234.1+547.241+541.128]

[Abstract] A study is presented of the influence of the structure of N,N-dimethylamides of dialkyl- and diarylphosphinic and phosphoric acids (I-VII) on their catalytic activity in the reaction of diphenylphosphinic acid hydrazide (VIII) with phenylisothiocyanate (IX) in benzene at 25° C. The reaction was found to be irreversible with formation of phosphorus-containing thiosemicarbazide (X). A stoichiometric equation is presented. The addition of small quantities of amides linearly increases the reaction rate. The catalytic interaction is quantitative and no secondary processes were observed. N,N-dimethylamides of organophosphorus acids have high catalytic activity in formation of thiosemicarbazides. The highest catalytic activity is that of N,N-dimethylamides containing alkyl radicals at the P = O group, reaching 4,331. A common base mechanism is suggested for the catalysis. References 17: 16 Russian, 1 Western.

### Organophosphorus Compounds Based on Substituted 2-Chlorocyclobutanones

937M0045D St. Petersburg ZHURNAL OBSHCHEY KHIMII in Russian Nov 91 pp 2566-2568

[Article by L. N. Grishina, O. Ye. Gayfullina, N. P. Dubinina, I. A. Nuretdinov; UDC 547.1.118+547.446]

[Abstract] A study is made of the reaction of functionally substituted alpha-chlorocyclobutanones with phosphorous acid esters, using products of the reaction of carboxylic acids with 7,7-dichlorobicyclo[3.2.0]hept-2-ene-6-one in the presence of triethylamine. The IR spectra of the compounds obtained have intensive absorption bands of the C = O group at 1790 and 1740  $\text{cm}^{-1}$ , with a weak C = C absorption band at 1608  $\text{cm}^{-1}$ . When heated with trivalent phosphorus acid esters these compounds liberate alkyl chloride and a reaction occurs forming the corresponding vinyl phosphates. The structure of the products obtained was confirmed by spectral methods and elemental analysis. Tables are presented of the yields, physical constants and analysis results of all compounds obtained. References: 8 Western.

**Coordination compounds of Co(II) With Sulfenamide Derivatives of 2-Mercaptobenzothiazole and Their Thermal Conversions**

937M0045E St. Petersburg ZHURNAL OБSHCHEY KHIMII in Russian Nov 91 pp 2589-2595

[Article by V. A. Karpinchik, A. I. Prisyazhnyuk, V. I. Nikitin, G. P. Sokhranenko; UDC 547.789.6-386:546.73]

[Abstract] The purpose of this study was to synthesize, investigate the stereochemistry and influence of substituents at the sulfenamide nitrogen atom on processes of thermal conversion of complexes of Co(II) with 2- benzthiazolyl sulfenamides(I-V). Elemental analysis of the compounds synthesized (VI-XIV) indicates that the presence of substituents at the sulfenamide nitrogen atom results in the production of complexes with composition 1 : 2. Changing the relationship of the components of the reacting substances has no influence on the composition of the products. The complexes are nonelectrolytes and their structure can be represented by the general formula  $\text{CoL}_2\text{X}_2$ . Diffractograms confirm the individuality of the coordination compounds synthesized. Thermogravimetric studies indicate that exothermic effects occur at 95-180°C on the DTA curves of the products with no corresponding mass losses on TG and DTG curves, indicating isomerization of the coordination compounds. The composition of the product after exothermic treatment was found to be identical to that before treatment. The substituents have a spatial influence on the reactivity of the compounds which is reduced by increasing temperature. A quantitative energy estimate of intramolecular restructuring was produced by computing the enthalpy of the process. Kinetic parameters of decomposition of the complexes and initial ligands were estimated, indicating that the activation energy of the decomposition reaction of cobalt complexes changes little with transition from chloride to bromide complexes. The formation of the coordination bond with the nitrogen atoms of the sulfenamide causes redistribution of electron density and changes the strength

of the Co-N bond, which increases with higher values of activation energy. Figure 1; References 11: 10 Russian, 1 Western.

**Interphase Catalysis in Tetrazole Chemistry**

937M0046A Riga KHIMIYA  
GETEROTSIKLICHESKIKH SOYEDINENIY  
in Russian Jun 92 pp 754-761

[Article by G. I. Koldobskiy, Yu. Ye. Myznikov, A. B. Zhivich, V. A. Ostrovskiy, V. S. Poplavskiy, St. Petersburg Institute of Technology]

[Abstract] The use of tetrazoles in medicine, biochemistry, agriculture, photography and particularly as components of data recording systems, has greatly expanded in recent years, due in no small part to the use of modern methods of physical chemistry in the study of tetrazoles and the latest synthetic methods for their production, including interphase catalysis. This review discusses the use of interphase catalysis in the synthesis of tetrazoles. Processes discussed include the synthesis of 1,5-disubstituted tetrazoles by the interaction of imidoylchlorides with hydrazoic acid or inorganic azides; synthesis of 1,3,5-trisubstituted tetrazolium salts by oxidation of 1,3,5-trisubstituted formazanes; alkylation of tetrazole and 5-substituted tetrazoles, a process which occurs in two stages with speed and selectivity depending on the electron structure of the substituents in position 5 of the tetrazole ring, nature of the alkylating reagent, nature of the counterion for tetrazole salt and reaction medium; acylation of 5-substituted tetrazoles for simple and effective synthesis of 2,5 disubstituted-1,3,4 oxadiazoles at high temperature in the presence of organic bases achieving high yields; and imidoylation of 5-substituted tetrazoles in pyridine at high temperature, forming 3,4,5-trisubstituted-1,2,4-triazoles. Tetrazolium salts have been shown to be catalysts for interphase transfer, equal in catalytic activity to tetrabutylammonium bromide and superior in thermal stability. Significant progress has been made in the past seven to eight years in studies of the reactions of tetrazoles under interphase catalysis conditions. References 53: 31 Russian, 22 Western.

### Turbulent Mass Transfer in an Axially Symmetrical Electrochemical Cell

937M0038B Moscow ELEKTROKHIMIYA in Russian  
Vol 28 No 5, May 92 (manuscript received 3 Dec 90)  
pp 681-686

[Article by T. N. Khomchenko, S. A. Martemyanov, L. N. Nekrasov, N. V. Petrovskiy, B. M. Grafov, Institute of Electrochemistry imeni A. N. Frumkin, Russian Academy of Sciences, Moscow; Moscow State University imeni M. V. Lomonosov; UDC 541.13]

[Abstract] Laws regulating turbulent mass transfer in the diffusion layers of the electrodes were studied under conditions of chaotic mixing of the electrolyte with a stirrer. A closed loop electrochemical cell with axial symmetry was used equipped with an electrode block located at the symmetry axis of the cell. The stirrer rotated at 3,000 rpm. Two approaches were taken in determining average limiting diffusion currents ( $I_d$ ) of the anion reduction over the electrode matrix consisting of 13 identical closely spaced platinum electrodes: in the first approach  $I_d$  was determined on each individual electrode with simultaneous polarization of all electrodes; in the second -  $I_d$  was determined on individual electrodes with polarization of only the electrode on which  $I_d$  was being determined. It was discovered that the currents on these electrodes were identical within about a 10% spread and that they did not depend on the distance of the electrode from the stirrer. Evidently, the surface of the electrode matrix located at the symmetry axis was equally accessible in respect to the diffusion to all electrodes. This could be possible only under conditions of the formation of a diffusion layer by turbulent pulsations of the electrolyte normal to their surface. Under such conditions the hydrodynamic conditions along the surface of the electrode matrix and throughout the cell were homogeneous. Tables 2; figure 1; references 15: 13 Russian, 2 Western.

### Capacity Characteristics and Impedance of Constant Phase Shift of Electrochemical Pb/KF-H<sub>2</sub>O Boundary

937M0038C Moscow ELEKTROKHIMIYA in Russian  
Vol 28 No 5, May 92 (manuscript received 22 Feb 91)  
pp 720-729

[Article by E. S. Sevastyanov, V. K. Chubarova, N. A. Morozova, E. V. Pekar, Institute of Electrochemistry imeni A. N. Frumkin, Russian Academy of Sciences, Moscow; Tula Polytechnical Institute; UDC 541.135.5]

[Abstract] Frequency characteristics of the active (R) and reactive (X) components of the impedance of a polished polycrystalline lead electrode were determined in a 0.01 M aqueous KF solution at potentials at which the electrode is normally considered to be ideally polarized. Frequency characteristics of the capacity and resistance on completely and partially reduced electrodes were then compared. Weaker currents and lower dispersions of X and R were noted on the reduced electrodes. In both systems the impedance of constant phase shifts was noted (ICPS). In case of ideally polarized electrodes the ICPS was explained on the basis of surface heterogeneity related to surface granularity. Frequency-independent capacity was calculated, equivalent to the capacity of double electric layer ( $C_D$ ). It was shown that an incomplete reduction of the electrode resulted in

lowered  $C_D$  values and in an increased heterogeneity of the interphase border. Capacity of the dense layer was calculated from  $C_D$  for the case of a negative surface charge on the reduced lead electrode and compared with mercury electrode data. Possible reasons for different capacities of the dense layer on Pb and Hg electrodes were analyzed for other electrode charges. Incomplete reduction of lead and granularity of the investigated electrode led evidently to opposite charges in the calculated capacity of dense layer. Figures 6; references 41: 19 Russian, 22 Western (4 by Russian authors).

### Electrochemical Behavior of Osmium Tetroxide in Acid Media

937M0038E Moscow ELEKTROKHIMIYA in Russian  
Vol 28 No 5, May 92 (manuscript received 16 Apr 91)  
pp 736-745

[Article by N. A. Kolpakova, L. A. Shvets, A. G. Stromberg, Tomsk Polytechnical Institute; UDC 541.138.3]

[Abstract] Literature data on the mechanism of electro-reduction of osmium tetroxide in acid media are contradictory. There are practically no data on the kinetics and ionization processes of osmium compounds on the surface of graphite electrodes. In this work the mechanism of discharge-ionization processes of osmium over a graphite electrode were investigated in H<sub>2</sub>SO<sub>4</sub> and HCOOH solutions. Two anode peaks were registered on a voltamperogram which were partially superimposable, and which the authors believed were related to a two step discharge-ionization process of osmium compounds. It was established experimentally that the first step in the electro-reduction of osmium tetroxide involved formation of an insoluble OsO<sub>2</sub> which then converted electrochemically to metallic osmium (IV). An algorithm was developed to separate these two peaks. A conclusion was reached that the electro-reduction and electro-oxidation processes in acid media are irreversible. Table 1; figures 8; references 26: 24 Russian (1 by Western authors), 2 Western.

### Characteristics of Electrochemical Reduction of Polytungstate Melts Under Excessive Pressure of Carbon Dioxide

937M0038F Moscow ELEKTROKHIMIYA in Russian  
Vol 28 No 5, May 92 (manuscript received 13 May 91)  
pp 779-784

[Article by Kh. B. Kushkhov, I. A. Novoselova, V. I. Shapoval, A. A. Tishchenko, Institute of General and Inorganic Chemistry, Academy of Sciences of Ukraine, Kiev; UDC 541.135.3:546.261:546.78]

[Abstract] Experimental results were reported of a voltamperometric investigation of the effect of carbon dioxide on electrochemical behavior of polytungstate melts. It was shown that carbon dioxide dissolved in the sodium tungstate melt and led to significant elevation of the concentration of tungsten dimer ions W<sub>2</sub>O<sub>7</sub><sup>2-</sup>. Discharge of these particles over a silver electrode occurs at potentials close to the potential of the separation of carbon and carbon dioxide. In the polytungstate melt containing WO<sub>3</sub>, the reduction potentials of W<sub>2</sub>O<sub>7</sub><sup>2-</sup> and CO<sub>2</sub> are superimposed and appear as a single reduction curve which results in formation of tungsten monocarbide. Cathode polarization

of tungsten carbide electrode in the system  $\text{Na}_2\text{WO}_4\text{-Li}_2\text{WO}_3\text{-CO}_2$  occurs without any noticeable overvoltage; this leads to the conclusion that the electrochemical synthesis of tungsten carbide in this system is a reversible process. Figures 6; references 9: 8 Russian, 1 Western.

**Calculation of Potential and Carrier Concentration Distribution During Current Flow in Electrochemical Systems With Fixed Charges**

937M0038H Moscow ELEKTROKHIMIYA in Russian Vol 28 No 5, May 92 (manuscript received 17 Apr 91) pp 809-811

[Article by A. V. Noskov, Yu. I. Kharkats, Institute of Electrochemistry imeni A. N. Frumkin, Russian Academy of Sciences, Moscow; UDC 541.135.5]

[Abstract] Theoretical description of the transfer of charged particles in solid electrolytic systems, in membranes or in films is normally based on simultaneous solution of the Nernst-Planck system of equations. In the present work theoretical analysis has been presented of the case where the current is carried by two type of charge carriers with opposite signs, while the system contains also charged immobile particles. Analysis of the formulas developed indicates that increased concentration of the fixed background and diminished ratio of the charges of mobile carriers lead to decreased limiting current  $f_i^l$ . A function was

calculated for limiting cation current  $f_i^l$  in respect to the anion current  $j_2$ . The function  $f_i^l(j_2)$  depends on the concentration of the fixed background and carrier charges. Figures 2; references: 5 (Russian).

**Additiveness of Influence of Halogens on Electrochemical Oxidation Potentials of Polyhalogen Benzenes**

937M0045B St. Petersburg ZHURNAL OБSHCHEY KHIMII in Russian Nov 91 pp 2400-2403

[Article by T. V. Magdesiyeva, V. N. Shishkin, K. P. Butin; UDC 547.539+541.138]

[Abstract] The electrochemical oxidation potentials of 17 polyhalogen benzenes containing F, Cl, Br and I were measured. A table of the data indicates that the ease of oxidation of hexahalogen benzenes is ordered as follows: F < Cl < Br < I. The same regularity is observed for  $C_6F_5X$  (where X = F, Cl, Br, I) although in  $C_6Br_5X$  the oxidation potentials are virtually independent of X, being determined primarily by the 5 bromine atoms. The halogen atoms influence the oxidation potential primarily through an inductive effect. The halogens are found to destabilize the cation radical in accordance with their (-I) effect, while the (+M) effect makes little contribution to the reaction. Figure 1; References 9: 3 Russian, 6 Western.

**Ozone Synthesis, Initiated by Nanosecond Corona in Air**

927M0228E Moscow KHIMIYA VYSOKIKH ENERGIY  
in Russian Vol 26, No 1, Jan-Feb 92 (manuscript received  
22 Oct 90) pp 76-81

[Article by R. Kh. Amirov, E. I. Asinovskiy, I. S. Samoylov,  
and A. V. Shepelin, High Temperatures Institute, Moscow;  
UDC 537.523.3]

[Abstract] Owing to the high costs of physical chemical methods of stripping stack gases of oxides of nitrogen and sulfur dioxide, electrochemical methods have been developed which employ an electrical discharge as well as electron pulses, such as in the electrofilters designed for use in coal dust operations where the dissociation products oxygen, water, and nitrogen are used for the cleansing operation. From an analysis of work on the use of pulsed corona to treat stack gases, it was concluded that the dissociation rate may be increased by shortening the pulse time and increasing the frontal slope. In the present work a study was made of ozone formation initiated by a nanosecond corona discharge in air at atmospheric pressure. Measuring the ozone concentration makes it possible to estimate the rate of oxygen dissociation and the energy consumed for the treatment. The dynamics of power consumption in the pulsed corona in relation to polarity, amplitude, and rate of voltage increase were determined. Experimental results were compared with calculations on the size of the corona model, and the efficiency of ozone synthesis as a function of the polarity and diameter of the corona electrode was determined. Figures 4; references 14: 6 Russian, 8 Western.

**Biometallic Complexonates - Derivatives of Dicarboxylic Acids - Ecologically Safe Plant Growth Stimulants**

927M0229E Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA - SERIYA 2 KHIMIYA in Russian  
Vol 26, No 1, Jan-Feb 92 (manuscript received 1 Mar 91)  
pp 60-63

[Article by I. B. Kovaleva, N. D. Mitrofanova, and L. I. Martynenko, Chair of Inorganic Chemistry; UDC 541.49]

[Abstract] One of the tasks associated with safeguarding the environment is the search for complexes which form compounds with metal ions that decompose rapidly in

living organisms or under refuse conditions. Very promising from the ecological standpoint are the derivatives of the dicarboxylic acids, viz. iminodisuccinic (IDS) and ethylenediamine-(N,N')-disuccinic (EDDS) acids. The EDDS complexon has been confirmed by structural reconstruction under relatively mild conditions. Inner molecular cyclization results in an almost irreversible loss of the complexon's ability to form chelate rings with metal ions, thereby decreasing the probability of ecologically dangerous shifts in ion exchange equilibrium when using EDDS for practical purposes. The purpose of the present work was to determine the changes that take place in complexonates of Cu(II) and Fe(III) derivatives of IDS and EDDS during ultraviolet photolysis of their aqueous solutions. Thin layer chromatography was used to identify the decomposition of the organic portion of the complex. It was demonstrated that UV-radiation results in destruction to form essential amino acids glycine, asparagine,  $\beta$ -alanine, isoleucine, and others. Figure 1; references 15: 10 Russian, 5 Western.

**Evaluation of the Ecological Effectiveness of Dust-Removal Systems**

937M0040A Moscow KHIMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE  
in Russian N 5, May 92 p 30

[Article by Doctor of Technical Sciences O.A. Troshkin and Candidate of Technical Sciences L.A. Tarasova: Evaluation of the Ecological Effectiveness of Dust-Removal Systems"; UDC 628.5.003.13:631.8]

[Abstract] The damage caused by atmospheric emissions is calculated by a simplified method in the form of the ratio  $U=gggd/M$  in which  $U$  is the damage caused by atmospheric emissions, rubles per year,  $g$  is 2.4 rubles/metric ton, a constant characterizing emissions into the atmosphere after 1985;  $g$  is a constant, a territorial indicator;  $d$  is a constant, a territorial indicator;  $f$  is a constant characterizing the dispersion of the impurity into the atmosphere; and  $M$  is the mass of the annual emission of contaminants from the source, standard metric tons/year. Damage from atmospheric emissions basically is determined by the passage of the solid phase in the dust-removal system and by the indicator of corrosiveness of the impurity. It is assumed that all components of the gas stream are captured to the same degree. A simplified equation is given for comparing dust removal systems for the same plant, in the initial parameters are identical. References: 2 Russian

**Effects of Low Temperatures, Radiation, and Deep Vacuum on Physical Chemical Properties of Polymeric Light-Absorbent Coatings**

927M0227A Moscow FIZIKA I KHIMIYA OBRABOTKI MATERIALOV in Russian No 2, Mar-Apr 92 (manuscript received 18 Jun 91) pp 26-30

[Article by V. V. Abraimov, N. N. Agashkova, I. V. Budnyak, A. A. Zakharova, N. I. Velichko, and A. M. Markus, Kharkov; UDC 539.61:539.043:539.211]

[Abstract] In the course of developing new devices for aerospace and cryogenic use, many new structural materials, such as polymeric composite and film materials, light-absorbent coatings, electric insulators, adhesives, sealants, and others found new applications. These devices operate under extreme conditions of deep vacuum, low temperatures, solar and ionizing radiation, etc. Therefore, at the present time the most important problem facing aero-space materials handling is across the board study of the physical mechanical properties of new materials subjected to the above factors for the purpose of ascertaining those processes taking place within the materials, and predicting the properties of these materials under extreme conditions. The purpose of the present work was to study the effects of corpuscular radiation (protons and electrons) with energies of 160 Kev, electromagnetic radiation at the 5-2,500 nm wavelength range, and the effects of thermal cycling at 4.2-300K temperature range on loss of mass, surface topology, optical and adhesive properties of fluoroplastic enamel FP-5246 on substrates of aluminum alloy AMG- 6 and stainless steel Kh18N9T. It was demonstrated that the above effects result in radiational modification of the optical properties of the light-absorbent coatings. A possible mechanism is surface etching of the coating from radiation. Also, the adhesive strength of the coating is lessened. The loss in mass of the coating as a result of radiation comprises 5 percent. Figure 1; references 6 (Russian).

**Features of Heating Finely Dispersed Ceramic Particles by Laser Radiation**

927M0227B Moscow FIZIKA I KHIMIYA OBRABOTKI MATERIALOV in Russian No 2, Mar-Apr 92 (manuscript received 5 Jun 91) pp 40-48

[Article by A. I. Bushma and I. V. Krivtsun, Kiev; UDC 551.573]

[Abstract] Increasing the efficiency of heating gas-dispersed particles has become an urgent problem in chemical synthesis, protective coating applications, and the technology of handling finely dispersed particles. The widely used method of heating particles in a high temperature gas stream (plasma) has low efficiency (2-4 percent). Heating by laser beam appears to be much more promising. While much work has been done on the heating of spherical particles in an electromagnetic field, the assumptions made regarding heat exchange (either from a stationary surface or uniformly distributed throughout the bulk of the particles) fail to take into account the space-time features of electromagnetic distribution of electromagnetic energy absorbed by the particles during laser heating. In the present work a study was made of some of the features of CO<sub>2</sub>-laser irradiation of finely dispersed particles of aluminum oxide, silicon dioxide, and titanium dioxide. A numerical analysis is

presented on the dynamics of heating the ceramic particles which takes the optical non-uniformity of the particles into account. Figures 5; references 17 (Russian).

**Applying Coatings by Reactive Magnetronic Atomization Under Direct Current**

927M0227C Moscow FIZIKA I KHIMIYA OBRABOTKI MATERIALOV in Russian No 2, Mar-Apr 92 (manuscript received 29 Apr 91) pp 87-93

[Article by Yu. G. Bushuyev, D. V. Rozinskiy, V. M. Prosvirikov, Ye. B. Malysheva, G. Yu. Aleksandrovskaya, and A. V. Kostyayev; UDC 621.793]

[Abstract] During recent years metallic oxide and nitride coatings have found broad applications in various branches of engineering. The method of reactive magnetronic atomization under direct current can be used for applying this type of coating, although researchers have encountered difficulties in connection with process control owing to the hysteresis effect in the current-discharge voltage relationship resulting in departure from parameters suitable for forming coatings. In the present work a theoretical and experimental analysis was made of the process of applying coatings of aluminum nitride and oxide by reactive magnetronic atomization under direct current. A model simulating magnetronic discharge in a mixture of inert and active gases was constructed and used to select criteria for reproducing conditions for film deposition of the above compounds, and a process control method is proposed. Figures 4; references 9: 2 Russian, 7 Western.

**Uniformity in Thickness of Coatings Applied by High Frequency Magnetronic Atomization**

927M0227D Moscow FIZIKA I KHIMIYA OBRABOTKI MATERIALOV in Russian No 2, Mar-Apr 92 (manuscript received 14 Mar 91) pp 94-98

[Article by V. I. Koba, I. V. Lunev, and V. G. Padalka; UDC 621.793.1]

[Abstract] The high frequency method of ionic atomization makes it possible to form various types of coatings by atomization on metallic, semiconductor, or dielectric targets without significant stoichiometric change. However, the low degree of ionization in the plasma discharge, and the correspondingly low ion density current on the target and low growth rate of the coating, often results in inefficient use of this method. The transverse magnetic field in the discharge zone, as created in magnetronic systems of ionic atomization, makes it possible to significantly increase plasma ionization from the Hall current of the electrons in the crossed electric and magnetic fields. The growth in degree of plasma ionization and the increase in current density on the target are accompanied by a significant increase in target erosion rate and a corresponding increase in coating formation rate. Thus, using the magnetronic system significantly raises the efficiency of high frequency ionic atomization making it one of the most promising methods. In the ion energy range of 0.5-1.5 kev, bombarding targets in systems of high frequency magnetronic atomization, exists a powerful relationship in the angular distribution between the particles of target material emitted from the target and from the ion energy bombarding the target, which may have a strong effect on thickness variations in

the resulting coating. In the present work a study was made of the effects of the geometry of a high frequency planer type magnetron having a circular target, the functions of the angular distribution of the target-emitted atoms, and the working gas pressure on the uniformity of film deposition on a substrate surface. It was demonstrated that by using a planer type magnetron with an annular target emission zone, the thickness variations in the resulting coating along the radius of the substrate depend little on either the function of the angular distribution of target atom emission, or on changes in the relationship between the width and mean radius of the target erosion zone. Figures 3; references 8: 7 Russian, 1 Western.

### Phase Equilibria in Systems Palladium-Platinum-Molybdenum and Palladium-Platinum-Tungsten at 1000°

927M0229D Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA - SERIYA 2 KHIMIYA in Russian Vol 26, No 1, Jan-Feb 92 (manuscript received 1 Mar 91) pp 57-59

[Article by S. V. Neuymina, G. P. Zhmurko, K. B. Kalmykov, Ye. M. Sokolovskaya, and V. N. Kuznetsova, Chair of General Chemistry; UDC 699.017.11.21/23]

[Abstract] Double diagrams of state of palladium and platinum with molybdenum and tungsten systems have been studied previously. No intermediate phases exist in the palladium-tungsten system, while in the palladium-molybdenum system two intermediate compounds are formed. During reaction of platinum with molybdenum five intermediate phases are formed. The platinum-tungsten system has not been well studied. In the present work diffusion pairs and equilibrium alloys were used to study the reactions of platinum and palladium with molybdenum and tungsten and isothermal cross sections of the systems palladium-platinum-molybdenum and palladium-platinum-tungsten at 1000° were constructed. Figure 1; references 8: 3 Russian, 5 Western.

### Wear Resistant Anodes With Textured Platinum Coating

937M0038A Moscow ELEKTROKHIMIYA in Russian Vol 28 No 5, May 92 (manuscript received 23 Jan 91) pp 675-680

[Article by E. V. Kasatkin, Ye. B. Neburchilova, N. G. Sedelnikov, A. M. Fatyushin, Scientific Research Physical-Chemical Institute imeni L. Ya. Karpov, Moscow; State Central Scientific Research Design and Construction Institute of Noble Metals and Diamonds, Moscow; UDC 541.135.5]

[Abstract] The structure and morphology of fine platinum coatings obtained by using atomized metal was investigated looking for the effect of plasma forming gas and of the type and structure of the coatings. Using the methods of x-ray structural analysis, electron microscopy and diffraction analysis of the reflected fast electrons, the structure and texture of these anodes with textured platinum coating were evaluated. Impulse potential-dynamic measurements, polarization, balance and corrosion determinations were carried out on electrodes with different textures under conditions of the synthesis of ammonium peroxydisulfate with evolution of

oxygen from the sulfate solutions. The yield of ammonium peroxydisulfate over textured coatings was 15-20% higher than over the non-textured material. Textured platinum-titanium anodes exhibited increased resistance to corrosion in the electrochemical process studied. Thus it was shown to be possible to intensify electrochemical processes by regulating the texture of the anode material. Promising electrodes with highly selective platinum coatings with necessary texture were developed assuring maximum yield of the final product with minimal loss of the noble metal. Tables 2; figures 5; references 5: 4 Russian, 1 Western.

### Study of the Radiation Stability of Semiconductor Cryogenic Thermal Converters of the TPK Type

937M0039A Moscow KHIMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE in Russian N 6, Jun 92 pp 20-24

[Article by Candidate of Physical-Mathematical Sciences A.B. Aleynikov and Candidates of Technical Sciences V.Ye. Borodin, S.P. Plotnikova, I.Yu. Nemish, V.N. Pantleyev, V.V. Plotnikov, and V.I. Cukhov]

[Abstract] Temperature sensors of the TPK type (USSR 839,369) intended for use in superconducting magnetic systems are subject to powerful ionizing radiation under cryogenic conditions. These sensitive elements of cryogenic semiconductor thermal converters are obtained by multi-component alloying of germanium by the zonal recrystallization method. The Sb, Ga, As, Se, and Au impurities added in different concentrations have different levels of ionization energies, and this determines the temperature range of each type of thermal converter. The Ga, As, and Se impurities are distributed in the crystal with a high degree of homogeneity, but their mass concentrations are determined by the integral fluence of the neutrons and isotopic composition of the original germanium crystal types. TPK-220 (from 60 to 100 K), TPK-420 (from 10 to 30 K), and TPK-720 (from 3.5 to 20 K) were tested for measuring temperatures under ionizing radiation condition up to 2 Mrad. The character of the change in the radiation correction of gT is reported graphically. The effect of radiation is to increase the resistance in the whole temperature zone. Consequently, the correction of gT has a positive sign. The error could be reduced by improving the technology of thermal sensitive material manufacture and by control of the mass concentrations of impurities at the crystal growing stage. References: 7 Russian.

### Synthesis of High-Temperature Bi:Pb:Sr:Ca:Cu:O (1.7:0.3:2:2:3:Y) Superconductors From Chemical Plasma

937M0043A Minsk IZVESTIYA AKADEMII NAUK BELORUSSKOY SSR: SERIYA KHIMICHESKIH NAUK in Russian No 3-4, Mar-Apr 92 (manuscript received 14 Oct 91) pp 3-7

[Article by I.F. Kononyuk, V.A. Lomonosov and Yu.G. Zonov, Institute of General and Inorganic Chemistry, Belarus Academy of Sciences; UDC 54.057:538.945]

[Abstract] Phase transformations were assessed in relation to performance characteristics of Bi:Pb:Sr:Ca:Cu:O (1.7:0.3:2:2:3:Y) superconductor formed from a nitrate aerosol chemical plasma. The data demonstrated that the

succession of superconducting phases was essentially identical to the processes occurring in roasted melts. Heating in air at 870° K of a charge containing crystalline CuO phases and complex Ca and Sr nitrates resulted in the appearance of a  $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ -type phase. The latter underwent transformation into  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  at 1070° K. Synthesis of the heterogenous  $\text{Bi}_{1-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  superconductor ( $T_{\text{crit}} = 105\text{-}110^\circ \text{K}$ ) required a temperature of 1100-1120° K. Figures 2; tables 1; references 9: 3 Russian, 6 Western.

### Structural Features of Mn-Containing Carbon Fibers

*937M0043B Minsk IZVESTIYA AKADEMII NAUK BELORUSSKOY SSR: SERIYA KHIMICHESKIKH NAUK in Russian No 3-4, Mar-Apr 92 (manuscript received 23 Jan 92) pp 40-45*

[Article by N.V. Gulko, N.V. Kitikova, I.N. Yermolenko (dec) and O.A. Sycheva, Institute of General and Inorganic Chemistry, Belarus Academy of Sciences; UDC 547.458.81:634.0.813.4]

[Abstract] Mn-containing carbon fibers were formed by permeation of cellulose hydrate with solutions of different concentrations of potassium permanganate and manganese nitrate, chloride, acetate and sulfate for various lengths of times under conditions of carbonization. IR- and x-ray spectroscopies of the fibers demonstrated that the products were dependent on the duration of carbonization and concentrations of the permeating solutions. In general, however, the following metallic phases were identified:  $\text{MnO}$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{MnTiO}_3$  as well as  $\text{MnS}$ . Figures 3; tables 1; references 5: Russian.

### Properties of Mixed Polyamido/Polyaminoamidoacid Composite Films

*937M0043C Minsk IZVESTIYA AKADEMII NAUK BELORUSSKOY SSR: SERIYA KHIMICHESKIKH NAUK in Russian No 3-4, Mar-Apr 92 (manuscript received 06 Nov 91) pp 100-103*

[Article by E.T. Krutko, I.Yu. Globa, N.R. Prokopchuk and A.I. Volozhin, Institute of Physicoorganic Chemistry, Belarus Academy of Sciences; UDC 541.64:536.4]

[Abstract] An analysis was conducted on the physical properties of thin films formed from polyamido-(I) and polyaminoamidoacid (II) polymeric composites. The former were prepared by reaction of pyromellitic acid and 4,4'-diaminodiphenyl ether, and the latter from 3,3',4,4'-tetraaminodiphenyl ether with benzophenonetetracarboxylic acid in dimethylformamide. The results showed that tensile strength, deformability, thermal stability, etc. of the films was dependent on the conditions of synthesis of the polymers, their ratios in the composites, intrinsic viscosities of the monomers, concentrations and ratios of the original

components. Films with optimum characteristics were obtained by reacting monomers with specific viscosities of 0.68 and 0.75 for the I and II classes of composites, respectively. For example, composite films characterized by a I:II ratio of 1:10 withstood concentrated sulfuric acid for 1200 h at 20° C. Figures 1; references 4: Russian.

### Phonon Mechanisms in Structural Forces of Thin Liquid Films

*937M0106A Moscow KOLLOIDNYY ZHURNAL in Russian Vol 54 No 4, Jul-Aug 92 (manuscript received 31 Mar 92) pp 5-13*

[Article by L.B. Boynovich and A.M. Yemelyanenko, Institute of Physical Chemistry, Russian Academy of Sciences, Moscow; UDC 539.216.2]

[Abstract] A formal mathematical development is presented for phonon mechanisms underlying structural forces in thin (< 50 nm) liquid films, which relates the excited state to acoustic waves in relation to temperature. The approach was based on the fact that many macroscopic systems—at sufficiently low temperatures—behave in the thermodynamic sense as ideal gaseous quasiparticles, leading to the analogy that the phonon spectrum represents forces which hold solids together. The mathematical considerations were shown to explain in an adequate manner many experimental observations on the behavior of thin liquid films which can be attributed to the existence of phonons. References 32: 5 Russian, 27 Western.

### Liquid Flow in Proximity of Capillary-Osmotic Sliding

*937M0106B Moscow KOLLOIDNYY ZHURNAL in Russian Vol 54 No 4, Jul-Aug 92 (manuscript received 03 Feb 92) pp 24-31*

[Article by O.I. Vinogradova, Institute of Physical Chemistry, Russian Academy of Sciences, Moscow; UDC 541.18:532.66]

[Abstract] A mathematical analysis was performed on those cases of capillary flow in which sliding along the wall arises as a result of aberrations in adhesion. Sliding velocity at a given point in time was demonstrated to assume the expression  $M^{(mz)^2}$ , where the time-dependent variables M and m correspond, respectively, to the velocity and physical length of sliding. Over a long period of time M and m become independent of time and quasistationary movement is established as a result of diffusion forces. Analysis of the hydrodynamic factors indicates that in such cases movement is affected by superimposition of two independent currents in the capillary. These consist of a flow-through current and a purely circulatory motion of the liquid induced by the sliding phenomenon. These findings have obvious applications in studies on capillary osmotic and diffusion-phoretic phenomena. figures 4; references 14: 12 Russian, 2 Western.

**Radiolysis of Thin Layers of Polymers on Surfaces of Various Solids**

927M0228D Moscow KHIMIYA VYSOKIKH ENERGIY  
in Russian Vol 26 No 1, Jan-Feb 92 (manuscript received  
27 Jul 90) pp 49-53

[Article by M. A. Bruk and G. G. Isayeva, Physical Chemical SRI imeni L. Ya. Karpov; UDC 541(15+64)]

[Abstract] In studying radiation modification and resistance to radiation in composite materials containing inorganic fillers, one of the most important questions is the effects of the filler on the radiolysis of the polymer-matrix. These effects might occur along several different channels. One basic channel is the effect of the filler on the bulk structure of the matrix and therefore on the radiolysis mechanism. Another is related with the redistribution of absorbed radiation energy between the filler and the matrix in connection with possible variations in electron densities. A very significant channel for this type of effect could also be those radiation processes taking place during irradiation directly at the filler-matrix interface. In the present work a study was made of the radiolysis of various polymers on the surfaces of silicon dioxide, aluminum oxide, carbon black, and graphite. It was demonstrated that aerosil sensitizes radiational destruction of polymethylmethacrylate, while graphite and carbon black provide protection against this type of activity. Radiation grafting of polymethylmethacrylate on aerosil is relatively slow, while that of polystyrene is significantly more rapid than in bulk. Probable reasons for the observed effects are discussed. Figures 2; references 6 (Russian).

**Determination of Structure Defect Level in Polymer Composites**

927M0230A Moscow PLASTICHESKIYE MASSY  
in Russian No 2, Feb 92 pp 15-17

[Article by T. B. Boboyev, V. V. Filatov, and N. A. Nikoleyeva; UDC 678.686:546.26:539.2]

[Abstract] The structure and properties of composite materials as a rule depend on the structure and properties of the composite components, i.e. a polymer matrix and a fiber filler. The properties and state of the interface also becomes an important structural entity by providing a stress transfer mechanism from the matrix to the filler. Analysis of a wide range of mechanical, chemical, and thermal properties of polymer composites, fiber fillers, polymer matrices, and resulting interfaces shows that the thermal-physical characteristics of these composites are significantly higher than analogous data on polymer matrices, while the interfaces formed by their interaction occupy an intermediate position. To evaluate the extent of structural breakdown in a polymer composite, such as an epoxide carbon fiber, a method was adopted consisting of sequential thermal analysis and mechanical testing. Carbon fiber "Elur" was impregnated with EN-6 epoxy resin and the resulting composite, hardened at 170°C, had 75 percent degree of filling. Samples subjected to flexing were compared with pre-calibrated standards to determine degree of thermal breakdown. Figures 3; references 7: 6 Russian, 1 Western.

**Effect of Acoustics on Character of Molecular Movement in Epoxide Polymers**

927M0230B Moscow PLASTICHESKIYE MASSY  
in Russian No 2, Feb 92 pp 20-21

[Article by R. M. Sultanayev; UDC 678.686:539.2:534]

[Abstract] Energy response, or energy modification as it is sometime called, is one of the factors which may affect the process of structure formation and thereby determine to a significant degree the properties of a polymer. A system may be subjected to energy response either before or during polymerization or while reworking in fabrication. It has been specifically demonstrated that acoustic response during hardening of epoxide polymers results in a marked increase in strength (up to 50 percent) and a significant change in relaxation properties of the hardened system. In the present work a study was made of the effect acoustic response in epoxide polymers. Epoxide resin EP-20 having a molecular weight of 420 and 26 percent epoxide number was hardened with an aliphatic diamine with and without the presence of acoustic energy. The tangent of the angle of dielectric loss as a function of temperature was then studied. The results indicate that acoustic response during polymerization causes concentration of chemical bonds and thus a slight rise in the density of the system. This limits segmentation and group mobility and insignificantly decreases the density of physical bonds (in this case hydrogen bonds). This facilitates intensity of movement (especially in the glassified state), but still does not compensate for the limit in mobility caused by the first two factors. Figures 3; references 12 (Russian).

**Effect of Compression Stress on Characteristics of Substance Transfer in Graphite-Filled Polymeric Material**

927M0230C Moscow PLASTICHESKIYE MASSY  
in Russian No 2, Feb 92 pp 22-23

[Article by N. G. Kats, R. O. Chak, V. P. Starikov, and A. A. Shevchenko; UDC 678.5:620.1]

[Abstract] Under service conditions polymeric materials are subjected to a variety of stresses which affect their physical-mechanical properties. The physical-mechanical properties of polymeric materials have been well studied for tensile stresses where breakdown is a result of normal stresses. Under compression load, a material is subjected to tensile stresses applied in a plane perpendicular to the compression load. The behavior of brittle polymeric material during breakdown is largely determined by the presence of defects, micro-fissures, and their growth. Under compression, their role is insignificant since the fissures close. Although this type of stress is frequently encountered it has not been fully studied owing to the difficulty in selecting suitable dimensions of samples for testing and correct procedures thereof. In the present work a special device was developed for evaluating the effects of compression stress on the penetration rate of a substance into a polymeric material. The device permits simultaneous testing of a large number of samples in various aggressive media at normal and high temperatures. Samples of furan resin DG-2 containing 60 parts by weight of graphite were tested in distilled water, and 5 percent solutions of sulfuric, hydrochloric and acetic

acids at temperatures ranging from 20 to 70° C. As compression load was increased, the diffusion coefficient of the various media decreased to a certain minimum and then increased again. Apparently, the initial decrease corresponds to the closing of fissures. With increasing compression stress, the fissure re-open to allow penetration of the medium. A formula is presented for determining the service life of graphite-filled polymeric materials in the first stage of compression stress. Figures 2; references 6 (Russian).

#### **Activation by Extraction of Hydrolyzed Microlignin, Used to Modify Polymers**

927M0230D Moscow PLASTICHESKIYE MASSY  
in Russian No 2, Feb 92 pp 27-29

[Article by Ye. G. Lyubeshkina, N. A. Tarasova, T. V. Ivanova, I. N. Skiba, and A. I. Kashlinskiy; UDC 678.5:557.001.73]

[Abstract] Technical grade lignins are excellent modifiers, stabilizers, and fillers for polymers. However, their addition to primary or secondary crude polymer material is curtailed owing to the intense odor of the process at temperatures exceeding 150° C. Also, lignin in the polymeric material has less of a modifying effect than that calculated from the concentration of free radicals or paramagnetic sites in the initial product as determined by EPR. This inconsistency results from the fact that commercial grade lignin (especially alkaline and hydrolyzed) is a heavily contaminated product where the impurities mask the paramagnetic sites thereby decreasing their concentration in the polymeric composition and lessening the effective activity of any additives. The functional activity of paramagnetic sites in lignin powder may be intensified, following appropriate preparation and electromagnetic milling. The surface of the lignin powder may be activated by treating with corresponding solvents, i.e. extraction with water, acetone, or n-hexane. In the present work the extraction was carried out by a known method where the "quality" of the solvent was determined by the migration of low molecular weight matter from the lignin into the solvent at a temperature just below the boiling point of the solvent. Data on migration, spectrophotography of the extract, and EPR indicate that water is the most effective solvent. Physical mechanical testing of extracted and non-extracted lignin compositions showed that tensile strength and creep limit during elongation are practically the same for both, with values comparable with polypropylene, while relative elongation and Young's modulus are higher in compositions containing the extracted lignin. This is apparently due to the fact that the number of active surface paramagnetic sites is elevated in the extracted lignin. This effect has great practical significance since it permits increasing the quality of materials and fabrications by increasing the number of active radicals by altering process conditions and by addition of additives. Figures 3; references 6 (Russian).

#### **Increase in Polymers' Electric Conduction as a Result of the Implantation of Molecular Ions**

937M0005B Moscow DOKLADY AKADEMII NAUK  
in Russian Vol 324 No 1, May 92 (manuscript received  
14 Feb 92) pp 131-132

[Article by O.Yu. Posudiyevskiy, I.G. Myasnikova, and A.A. Chuyko, academician, Ukraine Academy of Sciences, Surface Chemistry Institute, Ukraine Academy of Sciences, Kiev; UDC 678.7:621.315.5]

[Abstract] Ion implantation has proved to be one method of producing electrically conductive polymeric materials.  $\text{BF}_n^+$  ( $n = 1, 2, 3$ ) ions were implanted into polyethylene terephthalate and polyimide films to produce electroconductive films. The ions were implanted at doses of  $1 \times 10^{16}$  and  $1 \times 10^{17}$  ions/cm<sup>2</sup>. The implantation of molecular ions resulted in an increase in the study materials' electric conduction ( $\sigma_e$ ) by 2-3 orders of magnitude. Maximum electric conduction was achieved in specimens of polyethylene terephthalate implanted with  $\text{BF}_2^+$  ions, which indicated that a chemical effect is at work in the study process. This effect was attributed to either a doping process or to the fact that boron is built into the lattice of the study structures instead of carbon (both processes would result in a change in electron density at the Fermi level and thus in a change in electrical properties). The effect observed only occurred at a specified dose ( $1 \times 10^{16}$  ions/cm<sup>2</sup>), which is to say at a specified density of the electroconductive phase in the polymer's structure, which underscores the effect of the structure of the chain of the starting polymer not only on the magnitude of  $\sigma_e$  of the material formed under the effect of an ion beam but also on the formation kinetics of the new structures. The studies further indicated that the  $\pi$ -conjugation that occurs does not percolate through the entire implanted layer and that the conductive inclusions are true islands in the dielectric matrix. Table 1; references 7: 3 Russian, 4 Western.

#### **Synthesis and Study of Block Copolymers of Polycaproamide + Polyethylene Glycol**

937M0010A Mytishchi KHIMICHESKIYE VOLOKNA  
in Russian No 3, May-Jun 92 pp 8-9

[Article by Kh. Kozert, V.G. Silantyeva, and L.N. Mizerovskiy, Ivanovo Chemical Technology Institute; UDC 54.057:(678.675.126.547.422)]

[Abstract] A block copolymer of polycaproamide with an average molecular mass of about 6,000 and polyethylene glycol with an average molecular mass of about 400 was synthesized in a miniflame under a stream of inert gas at 523 +/- 0.5 K. The synthesis process was implemented in two stages: First, a prepolyamide was produced by cationic polymerization of caprolactam in the presence of anhydrous  $\text{H}_3\text{PO}_4$ . Next, a specified amount of polyethylene glycol was added to the reaction compound, and the reaction was continued in a laminar mixing mode until a block copolyamide with the desired molecular mass was obtained. Studies of the new block copolymer confirmed that it has a structure that will make it possible to produce fibers with improved color and hygiene indicators. The new block copolymer was determined to have a density of 1,145 +/- 5 kg/m<sup>3</sup>, a degree of crystallinity of 40 +/- 4%, a melting point of 463 to 526 K, a relative melting heat of 0.73, a moisture absorption of 4.6 +/- 0.1%, and a dyeability of 4.2 +/- 0.1 g/kg. Figure 1, table 1; references 2 (Russian).

#### **An Investigation of the Shape of the Interface in Two-Layer Flows of Polymer Melts During Coextrusion**

937M0010B Mytishchi KHIMICHESKIYE VOLOKNA  
in Russian No 3, May-Jun 92 pp 11-13

[Article by V.P. Pervadchuk, V.M. Levin, A.R. Davydov, and V.A. Svistunov, Perm Polytechnic Institute and All-Union Glass Fiber Scientific Research Institute; UDC 531.542:532.135]

[Abstract] Researchers at the Engineering Center of Polymeric Optical Fibers of the All-Union Glass Fiber Scientific Research Institute conducted a theoretical and experimental study of the shape of the surface of the interface of polymer melts in the bilayer axisymmetric flows that occur in cylindrical channels of spinnerets during the production of optical fibers. The experimental studies were performed on an intermittent-type laboratory-commercial spinning unit designed so that the temperature and dimensions of the shaping spinnerets remained constant. Type PSM-115 polystyrene was used as the core of the material, and polymethyl methacrylate and dacryl-4B were used as the sheathing. The rheological properties of the melts were calculated in accordance with a previously proposed mathematical model and compared with those determined from the experiments. The comparison indicated that the theoretical model provides an adequate description of the changes in the shape of the interface surface of bilayer polymer melts in spinnerets during the formation of optical fibers. The nature of the changes in interface surface shape discovered was explained in terms of a previously developed model identifying three zones in the flow of fluids through spinneret channels. The first of these zones, in which changes in the conditions of the flow change the flow's velocity profile and where the current lines are not parallel to the channel walls, is termed a zone of stabilization or the initial leg of the flow. In the second zone, i.e., the steady-flow zone, the current lines are parallel to the channel walls and do not change their position throughout the channel's length. In the third zone the current lines curve once again on account of a change in the conditions of the flow beyond the channel. Increasing the rate at which the core material is fed through the spinnerets was found to cause changes in the pattern of the combined flow in the channel. The extent of these changes varied depending on the relative feed rates of core and sheathing materials used. Figures 3; references 4 (Russian).

#### The Properties of Fibers Based on Acrylonitrile Copolymers Formed From Highly Viscous Spinning Solutions

937M0010C Mytishchi KHMICHESKIYE VOLOKNA  
in Russian No 3, May-Jun 92 pp 27-29

[Article by K.E. Ergashev, Zh.A. Zgibneva, S.I. Slepakova, and A.L. Kamkina, Tashkent Textile and Light Industry Institute; UDC 677.494.745.32:539.412.1]

[Abstract] The properties of fibers based on acrylonitrile copolymers formed from highly viscous spinning solutions were studied. The spinning solutions were prepared from a ternary copolymer of acrylonitrile, methyl acrylate, and itaconic acid in a molar ratio of 92:6.4:1.6 (molecular mass, 40,000) and from a binary copolymer of acrylonitrile and methyl acrylate in a 94:6 molar ratio (molecular mass, 78,000). The effects that additions of isopropyl alcohol in amounts insufficient to cause cloudiness and gel formation (i.e., in amounts ranging from 2 to 18 wt.-%) have on the properties of the resultant fibers were studied. The lowest viscosities and spinning values were found when isopropyl alcohol was added in amounts of 6 and 12 wt.-%. The reduction in viscosity and spinning value obtained by adding isopropyl alcohol in 6 and 12% concentrations in turn caused a reduction in the elastic part of the fiber's deformation. After further studies, the researchers were able to increase the concentration of isopropyl alcohol to 14-15%

when forming binary copolymers based on acrylonitrile and methyl acrylate at the conventional process temperatures. The fibers thus produced had a measured strength of 600 to 770 mN/tex and an elongation stretch of 10%. Figures 2, tables 2; references 6 (Russian).

#### Oxidation and Co-oxidation of Polymers and Polymer Wastes in Solution

937M0011A Moscow PLASTICHESKIYE MASSY  
in Russian No 1, Jan 92 pp 26-28

[Article by A.M. Ivanov, Ye.N. Rozanova, I.A. Ivanov, and T.N. Kudryavtseva; UDC 678.7:66.092.94]

[Abstract] The possibility of developing an oxidation process to recycle polymer wastes was assessed by way of the example of destructive oxidation of type SKS-30 ARKPN butadiene-styrene rubber and butyl rubber. It was discovered that the composition and properties of the oxidate may be varied by altering the chemical nature of the rubber used for the oxidation process (for example, types SKB, SKD, SKI-ZS, DSSK, SKEP, etc.), the type of solvent (including individual xylools and mixtures thereof, toluene, octane, higher-molecular paraffins, perchloroethylene, methyl ethyl ketone, etc.), and the catalyst (salts of manganese, cobalt, and other transition metals and mixtures thereof), as well as by varying the process temperature (from 50 to 100°C) and the flow rate and bubbling intensity of the process air. The method and intensity of feeding in external heat also proved to be important. Combining the stages of dissolution of the starting elastomer and its destructive oxidation was found to be a feasible way of expanding the molecular mass distribution of the process products, and conducting the process under conditions of a continuous increase in the content of dry oxidate residue with automatic withdrawal of a portion of the solvent in the oxidation process was found to be a way of increasing the total degree of oxidation. The use of peroxide additives and the co-oxidation of rubbers with one another, as well as the co-oxidation of oxidates of elastomers with other organic compounds, were determined to be ways of controlling the polymer oxidation process. A soft temperature regimen (50 to 100°C) was found to preclude the formation of highly volatile products of deep and poorly controlled thermal destruction. In cases where the chemical activity of a polymer or polymer wastes during oxidation is low, it was deemed advisable to process the materials by co-oxidation entailing adding specially selected inductors to the starting mixture and then using semidrying oils to enable the resultant oxidate-composites to be used as inductors. The co-oxidation of plant oils of such polymeric materials and wastes as rosin, indene-coumarone resin, SPP oil-polymer resin, and lavsan wastes was also examined. The studies established that many polymers and polymeric wastes may indeed be co-oxidized with plant oil. It was discovered, for example, that the addition of indene-coumarone resin to drying oils and paints significantly improved their appearance and performance. The possibilities of adding the resin to plant oil are limited, however, because of its poor solubility. Co-oxidation of plant oil with indene-coumarone resin not only solves the solubility problem but also significantly improves the ecological parameters of the oxidation process. The co-oxidation of plant oils and a number of other fats of animal origin with POD oil also appears promising. The research conducted thus demonstrated that the oxidation and co-oxidation of

polymers and polymer wastes in solutions are both promising methods of obtaining composites for finishing operations in different sectors of industry. Figure 1, table 1; references 10 (Russian).

### Cold-Hardening Polymeric Composite

937M0011B Moscow PLASTICHESKIYE MASSY  
in Russian No 1, Jan 92 pp 32-34

[Article by A.B. Nasirova, E.S. Mamedova, and I.V. Gasanova; UDC 678.744.5.01]

[Abstract] A copolymer of monoacrylate oligooxypropylene glycol [APG] (molecular mass, 1,500-2,000) and styrene with an APG:styrene molar ratio of 100:70 was synthesized and studied from the standpoint of its hardening. n,n',n"-Triphenylmethane triisocyanate (leykonat) was used as a hardener. The composite was hardened at a temperature of 298 K for 24 hours. Degree of hardening was judged on the basis of gel fraction content as determined by extraction of a pulverized weighted sample (0.3 to 0.5 g) by acetone. A Specord 751R infrared spectrometer and ball viscosimeter were used to determine the samples' adhesion characteristics and viscosity. The extraction studies established that during study polyester's hardening, a space-network cross-linked insoluble polymer forms and that the process of the hardening of a hydroxyl group-containing polyester by means of an isocyanate hardener occurs in accordance with a migration polymerization mechanism resulting in the formation of urethane groups. The formation of a cross-linked polymer was further confirmed by differential thermal analysis. As the sample composites hardened, their viscosity increased and their content of NCO groups decreased. When the amount of hardener was increased, the composite's viscosity increased at a more rapid pace. After 50 minutes of hardening, the number of NCO groups in the sample composites decreased from 7.1 to 0.6%. This sharp decrease in viscosity was attributed to the formation of a structural mesh. The adhesion characteristics of the study composites was found to depend on the ratio of components constituting the individual composites. All of the specimens possessed a rather high adhesive strength, which was probably due to the urethane groups in the structure of the hardened specimens. Figures 2, tables 2; references 6 (Russian).

### The Effect of Fillers on the Rheological Properties of Binary Mixtures of Incompatible Polymers

937M0011C Moscow PLASTICHESKIYE MASSY  
in Russian No 1, Jan 92 pp 36-38

[Article by A.V. Savelyev, V.Ya. Kiselev, and I.A. Tutorskiy; UDC 678.743.46:033.01]

[Abstract] The rheological characteristics of binary mixtures of incompatible polymers are dictated primarily by the properties of the starting polymer components and by the level of reaction between them. Adding a filler to a polymer mixture can accomplish two things. First, a filler can modify the polymer phases depending on its distribution in the bulk of the mixture and thus change the phases' viscosity. Second, a filler can either increase or decrease the level of reaction at the interface between the incompatible phases. Fillers may be added in different ways. Adding a filler through the mother liquor makes it possible to intentionally

increase the amount of filler in one of the mixture's components, thus permitting selective modification of mixtures. Adding a filler through one of the polymeric components of a mixture or through both components simultaneously in a 50:50 ratio creates conditions for the transfer of one of the polymers of the mixture into a continuous phase, the distribution of filler between the two phases, and the transfer of the filler from one phase to the other upon mixing. The commercial rubbers PIB-200, NK, SKN-18, SKN-40, and SKU-8TB were studied along with polypropylene and type PA-6 polyamide to determine the effect of fillers and the sequence in which they are added to binary mixtures of incompatible polymers. Commercial-grade carbon, BS-50 white black, zinc oxide, aluminum powder, and F-4 ground fluoroplastic were used as fillers. A Tesla BS-413 electron microscope was used to study the structure of the study mixtures and the distribution of filler in them. When a small amount of filler was added to rubber mother liquors, their viscosity decreased on account of destruction of the polymer phase. As the content of filler was increased, the viscosity of the mother mixtures increased also. The viscosity of binary mixtures obtained by adding another rubber to the mother liquor changed accordingly. In most cases, minimum viscosity of the binary mixtures studied was observed at filler concentrations of 5 vol.-%. No consistent pattern developed when the different rubbers and fillers were added simultaneously. Each of the different starting substances studied behaved differently; for example, preliminary filling of polypropylene reduced its viscosity in all of the mother liquors studied, whereas mother liquors based on PA-6 with filler added to them had a higher viscosity than did the corresponding unfilled polymers. Simultaneous mixing of the components of the study binary mixtures did not have any significant effect on the mixtures' physicomechanical properties. Adding a filler to pre-prepared mixtures of incompatible rubbers having a large interface surface area resulted in the concentration of filler primarily at the interface. When such was the case, the degree of modification of polymer components of the mixture remained minimal, and the mixture's viscosity remained virtually unchanged regardless of the compatibility of the individual polymers or their volumetric ratio in the mixture. Figures 3, tables 2; references 6 (Russian).

### Calculating Geometric Parameters of Injectors To Pour Polymeric Composites When Producing Multilayer Structures

937M0011F Moscow PLASTICHESKIYE MASSY  
in Russian No 1, Jan 92 pp 47-50

[Article by V.I. Nikitin and V.V. Guryev; UDC 678.5-405.8.02.001]

[Abstract] An interactive simulation system (described elsewhere) based on a multifactorial mathematical model was developed to solve the problems entailed in controlling the process of injecting foamed polymers when manufacturing multilayer structure, as well as to design the equipment required for the process. This interactive system may be used to solve diverse problems related to injecting foamed polymers; however, a rather laborious computer experiment is required. In the interests of simplifying the injector design process, the authors of this article have developed approximate formulas and substitute nomograms that may be used to determine the critical geometric parameters of tubular

injectors for injecting polymeric composites when producing layered panels by the bench and continuous methods. The formulas and nomograms are based on data from a computer experiment and reflect the effect of the most significant factors on the maximum possible (critical) length of the perforated portion of the injector and the maximum possible diameters of all its openings spaced at identical increments. Two detailed examples are provided to illustrate the use of the five expressions presented when designing injectors to be used in producing panels by the bench and continuous methods. Figures 3; references 3: 2 Russian, 1 Western.

### The Use of Polymers of Lignin and Its Derivatives (A Review)

937M0011G Moscow PLASTICHESKIYE MASSY  
in Russian No 1, Jan 92 pp 56-61

[Article by V.N. Zaplishnyy, Yu.N. Moysa, N.S. Kotlyarov, and V.A. Moysa; UDC 678.557.004.14]

[Abstract] The processing of wood and products of plant origin in the hydrolysis and pulp and paper industries results in by-product hydrolytic lignin, lignosulfonic acids, oxidized lignin, and other compounds. The volume of lignin generated amounts to as much as one-third of the wood processed. Traditionally, this lignin has largely been used in unmodified form as boiler fuel or for agricultural purposes. In the past 10 years, a great many publications have examined ways of using by-product lignin and lignin derivatives, improving methods of processing them, and finding new areas in which they may be used. A sizable number of these publications focus on the composition of lignin-based polymers and methods of producing them, including such methods as sulfiding and graft copolymerization. Most of the research in the field of lignin- and lignin derivative-based polymers is devoted to their use. Polymers based on lignin and its derivatives may be used as fillers when manufacturing polymeric composites (especially thermoplastics) and have been used successfully as additives to various building material mixtures (cements, concretes, molding and injection mixtures, ceramics, etc.). Commercial-grade lignosulfonic acids may be used in self-hardening mixtures and binders in foundry work. Thanks to their good adhesive characteristics, lignin-containing composites may be used in adhesives, binders, and foamed plastics. Even without further processing, solutions of lignosulfonic acids have a much higher wettability than water does with respect to coal dust and may be used as dispersing agents and surfactants. Modified lignin is highly suitable for use in rust converters and inhibitors of salt deposition. Several lignosulfonic acids have been found to have electroconductive and polyelectrolyte effects. Lignin and lignin derivatives also have important agricultural applications. They may, for example, be used in soil stabilizers, fertilizers, and bioactive agents. Commercial-grade hydrolytic lignin and lignosulfonic acid may be used successfully as sorbents for extracting metal ions from sewage. Lignin- and lignin derivative-based polymers may also be used as modifiers for drilling fluids, grouting mortars, and polymeric composites. The problems of recovering lignin and extracting residual quantities of lignin and lignosulfonic acid from aqueous solutions have yet to be solved definitively; however, several

promising techniques have recently been studied, including complexing and composting. References 139: 99 Russian, 40 Western.

### The Status and Problems of Realizing the Gold Potential of the CIS Under the Conditions of a Market Economy

937M0012A Moscow SOVETSKAYA GEOLOGIYA  
in Russian No 3, Mar 92 pp 4-11

[Article by B.I. Benevol'skiy, I.F. Migachev, and Yu.M. Shchepot'yev, Central Geological Prospecting Scientific Research Institute; UDC 553.003.1:553.411]

[Abstract] Russian, Uzbekistan, and Kazakhstan are the three countries of the CIS with the greatest gold reserves, forecast gold (placer and vein) resources, and complex gold-containing nonferrous metal deposits (copper-porphyrific, copper-nickel, polymetallic, etc.). The former USSR ranks second in the world with respect to prospected gold reserves and amount of gold recovered but only ninth with respect to gold production. Thanks to a series of investments and measures to strengthen the gold recovery industry, total gold reserves increased by a factor of 1.5 between 1970 and 1985. Lately, however, economic problems have forced a slowdown in the pace at which the gold raw material base of the CIS is being developed. Nearly half the gold recovered in the former USSR has been placer gold, and overall 60% of all gold recovery enterprises lack an adequate raw material base. Preparing placer deposits for recovery requires significant monetary and physical expenditures and creates a number of ecological problems. About 35% of all vein deposits (27% of the reserves) are now being worked, about 4.5% (10% of the reserves) are being prepared for assimilation, and the remainder are being held in reserve or else not slated for assimilation because of technical and/or economic considerations. Overall, the raw material base of gold ore deposits is adequate; however, it is inadequate for two-thirds of existing enterprises. About one third of all ore mines have a depleted raw material base. More than 300 vein deposits have been prospected, however, and gold output from vein deposits could be doubled if they were to be mined. In Uzbekistan, the recovery of gold from vein deposits has risen to nearly half the union's entire output. Russia, on the other hand, is experiencing serious problems with its raw material base because it has to date built only one small enterprise devoted to the task (i.e., the Karamken GOK). In order to maintain the growth in her gold recovery industry, Russia must realize the great potential of her vein deposits. Above all, construction of large and medium-sized enterprises to assimilate gold ore deposits must be accelerated. The key to the problem is assimilating the Sukhoy Log deposits in the Irkutsk Oblast. Radical measures must also be taken to assimilate large deposits (the Nezhdaninskoye, Mayskoye, Olimpiadinskoye, Kyuchus, etc.) containing ores that are technologically difficult to recover because their processing currently results in arsenic formation. The problems related to assimilating small gold deposits must be addressed quickly (for example, by completing work on module-based equipment and technologies now under way at the Central Geological Prospecting Scientific Research Institute. Obtaining a correct value estimate of the gold deposits of the CIS is another critical problem. In view of the above problems, the following measures should receive highest priority: 1) construct ore

enrichment combines at a number of deposits (above all in Russia) as quickly as possible so as to double the yearly recovery of gold from vein deposits; 2) continue intensive prospecting and estimation operations at placer deposits in southern Siberia and in as-yet unexplored regions (the Polar Urals, Taymyr, Lake Bolshevik, the northern part of the Kamchatka Oblast, etc.); 3) introduce the technology of processing rush gold ores; 4) intensify the study and prospecting of deep horizons and new types of ores within the confines of fields now being worked; and 5) concentrate the search for new gold deposits in regions with an existing mining industry, where such searches will have maximum economic efficiency. Figures 4, table 1.

### The Orapa Weakly Eroded Kimberlite Pipe

*937M0012B Moscow SOVETSKAYA GEOLOGIYA  
in Russian No 3, Mar 92 (manuscript received 29 Oct 90)  
pp 14-21*

[Article by A.D. Kharkiv, A.F. Safronov, and G.I. Smirnov, Central Geological Prospecting Scientific Research Institute; UDC 552.323.6(571.56)]

[Abstract] Samples of kimberlites taken from three depths (300 m, 30 m, and 10-15 m) of the Orapa pipe in Botswana were studied. The study data, combined with previously published information on diamond eclogite and graphite eclogite xenoliths of the Orapa pipe, were used to develop a general profile of the pipe and detail the chemical composition of its minerals. The available data confirmed that the upper horizons of the Orapa tube consist of crater facies rock with a reduced diamond content. The said deposits contain the traditional kimberlite minerals, especially chrome diopside, chloritized phlogopite, and rare grains of pyrope and picroilmenite. This complex of minerals is said to be a diagnostic indicator of crater facies rock in cases where they are hard to distinguish from conventional sedimentary formations. Overall, crystals of eclogite paragenesis predominate among the diamonds of the Orapa pipe. An ultrabasic paragenesis of minerals is found to predominate in a small class of concentrates from the pipe, however, and the main correlative links between the amounts of diamonds and knorringite-pyrope garnets of diamond association are maintained. The data obtained in the study of samples from the Orapa pipe thus confirm the universality of the mineralogical criteria developed by N.V. Sobolev. The available data regarding the fact that African kimberlites rarely contain xenoliths of ultrabasites of pyrope-diamond facies containing garnets of diamond association, the adjusted amounts of garnets of diamond association contained in the kimberlite cement of the Orapa pipe, which has a relatively high diamond content, and available data regarding the distribution of garnets of this type in other diamond-bearing pipes of the region all indicate that the kimberlites of South Africa contain a lesser amount of garnets of diamond association than do the Yakutia and Eastern European kimberlites. This is evidently another typomorphic feature of the diamond-bearing kimberlites of South Africa. Figures 3, tables 2; references 10: 4 Russian, 6 Western.

### The Synthesis and Conformation Characteristics of a Copolymer of N-Vinylpyrrolidone + Acrylamide

*937M0013B Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 1, Jan-Feb 92 (manuscript received 20 Feb 91) pp 44-48*

[Article by Kh. Zayirov, U.M. Mirzayev, T.M. Mirkamilov, F.T. Abdullayev, and E. Urinov, Tashkent Friendship of the People Order Polytechnical Institute imeni Abu Raykhana Beruni; UDC 541.64:547.39]

[Abstract] Copolymers of N-vinylpyrrolidone and acrylamide with N-vinylpyrrolidone:acrylamide molar ratios of 0.5:0.5 and 0.7:0.3 were synthesized at temperatures ranging from 40 to 70° C in the presence of the initiator dinitrile of azoisobutyric acid. The study copolymers were white powders that proved to be soluble in water and ethyl and methyl alcohols but not in acetone, dioxane, and benzene. Fractionated samples of the N-vinylpyrrolidone-acrylamide copolymers were studied by rapid sedimentation and viscosimetry in water. The composition of the starting mixture proved to be the main factor dictating the product yield, with the copolymer yield increasing as the amount of acrylamide in the reaction mixture was increased. The biggest increase in yield was achieved at 60° C, at which point conversion after 4 hours reached 77% with an N-vinylpyrrolidone:acrylamide ratio of 0.5:0.5 and 55% with an N-vinylpyrrolidone:acrylamide ratio of 0.8:0.2. As expected, increasing the concentration of initiator and the duration of the reaction also resulted in increased yields of the copolymer. Infrared spectroscopy comparisons of the study monomers and copolymers confirmed that the copolymerization entails breaking of the double bond. Figures 5, table 1; references 7: 6 Russian, 1 Western.

### Sanitary-Chemical Study of Two-Layer Self-Adhesive Polymer Film Containing Lincomycin

*937M0017A Yerevan ARMYANSKIY KHIMICHESKIY ZHURNAL in Russian No 7-8, Jul 91 pp 472-476*

[Article by A. V. Gazaryan, O. P. Sotskiy, K. M. Kocharyan, G. A. Oveyan, L. V. Sukiasyan, F. A. Sarkisyan, G. A. Chukhadzhyan and Sh. A. Kazaryan, Yerevan State Medical Institute imeni M. Geratsi; UDC 66.11:538.6]

[Abstract] The authors previously developed a technology for producing a bilayer self-adhesive film containing a hydrophobic and a hydrophilic layer which adheres to injured areas of organs upon contact. The composition of the hydrophilic film layer allows a number of medications to be included in the film which, bonding covalently or by adsorption with the polymer matrix of the hydrophilic layer, slowly migrate outward, creating a high local therapeutic level of the medication. This article describes a sanitary-chemical investigation of this film, called diplene, containing lincomycin to determine the possibility of its use in medicine. Experiments were performed with diplene film containing lincomycin in order to determine the agreement of the properties of the film with the standards and requirements placed upon polymers designed for use in medicine. Specimens were treated in water and a 4 percent solution of acetic acid, immersed in a liquid with a temperature of 60° C for 30 minutes, and the content of phenol, formaldehyde

and heavy metals, uptake of potassium permanganate and residue after evaporation of a solution were determined. The films are found to satisfy the requirements of the standard for medical use. Further studies investigated the dynamics of migration of the antibiotic from the films using distilled water as the model medium. Most of the lincomycin was found to migrate into the water within the first 3 days, only 7.03 percent remaining as long as 7 days and virtually no antibiotic being detected at 21 and 30 days. The sanitary-chemical properties are considered satisfactory for use in medical practice. References: 5 Russian.

#### Polymer Composite Materials Based on Polyether Esterketones (Review)

937M0018A Moscow PLASTICHESKIYE MASSY  
in Russian No 3, Mar 92 pp 3-7

[Article by A. Kh. Shaov, A. M. Kharayev, A. K. Mikitayev, G. S. Matvelashvili, Z. S. Khasbulatova; UDC 678.674.01]

[Abstract] Polyether esterketones (PEEK) are excellent high-temperature structural materials, with long-term usage temperatures of composite materials containing 30 percent carbon fiber as high as 240° C. This review of the [entirely Western and Japanese] literature discusses the structure, properties, manufacturing methods, testing and use of PEEK. The influence of heat treatment during manufacture on strength of carbon-reinforced PEEK composites is discussed. Pump parts made of pressure-cast PEEK composites have a service life of 18 months in hot, corrosive environments, as opposed two months for epoxy-based parts. Layers of graphite fibers, steel fibers, nickel flakes and other conducting fillers can yield low-cost, highly conductive parts. Annealing of specimens near the melting point for several days helps to make composite part properties uniform throughout the cross section. Shortcomings of PEEK include high cost, low fluidity and high melting point. Addition of polyether sulfone reduces flammability while retaining good strength at up to 200° C. Composites based on PEEK and polyphenylene sulfide have very low vacuum mass loss and liberation of volatiles under a vacuum, meeting the requirements for space equipment. Another problem of PEEK is its high coefficient of friction. Polyethylene terephthalate can be introduced to improve tribologic properties. PEEK is stronger than epoxy resin and more resistant to proton bombardment, electrons and UV radiation, and also to cyclical heating and cooling from -156 to +180° C and thermal shock as tested by exposure to liquid nitrogen and helium. Further improvement in PEEK composite properties can be expected in the near future. References: 71 Western.

#### Rheology and Strength of Transversely Isotropic Polymer Bodies

937M0018B Moscow PLASTICHESKIYE MASSY  
in Russian No 3, Mar 92 pp 16-18

[Article by S. A. Yelsufyev; UDC 678.7:532.135:539.376]

[Abstract] A theoretical method which considers processes of deformation and crack formation before fracture is used to estimate the deformation resistance of transversely isotropic materials, as well as the strength of a plate and thin wall specimen with planar loading. Rheologic equations are presented which can be used, together with the criterion of

infinite elongation rate at the moment when localization begins in a plate under biaxial extension, to estimate the ultimate strength of structural elements and to derive theoretically the fracture conditions of an element of the material. Analysis of the equations presented confirms the influence of the shape of a structural element on the nature and time of its transition to unstable deformation under load. Theoretical and experimental results are in agreement. Figures 2; references: 2 Russian.

#### Basic Equation for Annealing of Crystalline Polymers

937M0018C Moscow PLASTICHESKIYE MASSY  
in Russian No 3, Mar 92 pp 19-20

[Article by A. M. Aryev; UDC 678.675.029.73]

[Abstract] An equation is derived to describe the process of secondary crystallization which occurs during annealing of polymers. The crystallinity of a polymer can increase as long as its temperature is held within the crystallization range of the specific polymer, either by nucleation of new crystallization centers, or by radial growth of existing crystalline centers. Components in the equation consider each of these two factors in the growth of crystallinity in a polymer during annealing. The equation can be used to predict the change in the degree of crystallinity of polymers during annealing and thus predict the physical properties. References 12: 10 Russian, 2 Western.

#### Structural Parameters of Perfluoromethacrylic Acid Fluoride Copolymers with Fluoroethylene

937M0018D Moscow PLASTICHESKIYE MASSY  
in Russian No 3, Mar 92 pp 20-21

[Article by F. Z. Yusupvekova, M. N. Rakhimova and M. K. Asamov; UDC 678.743.41-13:539]

[Abstract] A study is made of the influence of perfluoromethacrylate links of perfluoromethacrylic acid fluoride with side COF- and CF<sub>3</sub>-groups on the structural parameters of fluoropolymers, such as crystallinity, density and molecular packing. The interrelationship of these parameters with the Van-der-Waals volume of the comonomers is considered. Studies were performed on double and triple copolymers with vinyl fluoride, vinylidene fluoride and tetrafluoroethylene. Addition of the acid fluoride to trinary copolymers causes nonadditive changes in copolymer density, significant amorphization and a decrease in chain molecular packing density. Thus, the crystallinity, molecular packing and nonadditive density alteration are closely related to the Van- der-Waals volume of the monomer elements and their arrangement in the copolymer chain. References: 5 Russian.

#### Influence of Thermal and Thermal-Moisture Aging on Electrical Properties of Polymer Materials

937M0018E Moscow PLASTICHESKIYE MASSY  
in Russian No 3, Mar 92 pp 23-24

[Article by S. I. Petrukhnenko, V. I. Sergeyev and G. A. Sutyrina; UDC 678.743.46.019.391:537]

[Abstract] The electrical properties of composite materials based on Polyamide, propylene, polybutylene phthalate

and polyoxymethylene were studied before and after aging at high temperatures and humidities in order to determine the influence of aging condition on the dielectric properties of these composite materials. Tests were performed on disk-shaped specimens 50 mm in diameter and 2 mm thick at a test voltage of 1000 V to determine resistivity and dielectric strength was determined on the same specimens with smoothly rising voltage in transformer oil. The materials were thermally aged at 60, 100, 130 and 150° C, and aged at 40° C and 96% relative humidity and at 60° C and 80% relative humidity. The electrical properties of all the materials were found to remain at their initial level after aging. The greatest reduction in dielectric properties were observed in PA, while polyoxymethylene material type SFD had the greatest stability of electrical properties under all aging conditions. All the materials except for the PE material can be recommended for use at high temperatures.

Figure 1; references: 5 Russian.

#### Influence of Titanium Salicylalimine on Epoxy Polymer Properties

937M0018F Moscow PLASTICHESKIYE MASSY  
in Russian No 3, Mar 92 pp 28-30

[Article by A. V. Kurnoskin and M. Z. Kanovich; UDC 678.686.043:546.821]

[Abstract] Titanium salicylalimine, or titanium hydrosalicylamide (THSA) is a compound of the empirical formula  $TiC_{21}H_{15}N_2O_4$ ,  $nC_{21}H_{18}N_2O_3$ , ( $n = 1-1.5$ ). THSA is a product of the condensation of salicylaldehyde with titanium trichloride and an aqueous solution of ammonia. Various epoxy oligomers were tested, with THSA introduced by reaction with amines which were heated to the melting point, followed by addition of the chelate to the melt. Mixing of the modified hardener melt with the oligomer at 50-60° C yielded the titanium-containing epoxy-chelate composition. The influence of THSA on the gel-formation time was studied and found to have an accelerating effect, reducing gel-formation time by a factor of 2-10 by decreasing the nitrogen-hydrogen bond strength in  $NH_2$  groups of aromatic amines. The properties of the epoxy polymers were compared with those of polymers containing copper salicylate and triethanol aminotitanate. The addition of the chelate rings was found to increase deformation thermal stability and thermal oxidative stability of the polymers significantly. The anions were found to influence elastic-strength characteristics, the cations influencing primarily the thermal stability of the polymers. Figure 1; references 10: 7 Russian, 3 Western.

#### Influence of Liquid Media on PE Fatigue Wear

937M0018G Moscow PLASTICHESKIYE MASSY  
in Russian No 3, Mar 92 pp 33-34

[Article by V. P. Yartsev; UDC 678.742.3:539.538]

[Abstract] Fatigue wear, accompanied by flaking of individual surface areas, is of the greatest danger for friction of polymers. This article studies the influence of liquid active media on the wear of polyethylene. The wear rate of the PE was computed by means of an equation relating the fatigue wear rate as a function of pressure and temperature. It was found that the liquid media studied, acetone and an alcohol furaciline solution, significantly reduced the wear rate of

PE, from 2,000 to 71-100 mg/hr under the test conditions. Figures 2; references 4 Russian.

#### Influence of Curing Method of Siloxane Block Copolymers on Protective Properties

937M0018H Moscow PLASTICHESKIYE MASSY  
in Russian No 3, Mar 92 pp 37-38

[Article by L. N. Pankratova, V. B. Nesterov and O. Yu. Panov; UDC 678.842-13:678.026.01]

[Abstract] An estimate is produced of the possibility of using gamma radiation to cure thin-layer siloxane coatings based on block copolymers, designed to protect aluminum coatings in the manufacture of microcircuits. The studies were performed on oligosiloxane block copolymers containing flexible blocks of  $[(CH_3)_2SiO]_n$  and rigid blocks of the formula  $[(C_6H_5SiO_{1.5})_0(C_6H_5SiO(OH))_1]_m$ . The ratio of flexible to rigid blocks was 20:5, 20:10, 40:10 and 40:20. The protective properties of the siloxane compounds were estimated on test MOS structures coated with a film of  $SiO_2$ , on the surface of which strips of aluminum 20 m wide with a total length of 18.5 mm were produced by photolithography. Various organosilicon materials were found to react differently with the  $SiO_2$  surface. Heat-cured specimens had little protective effect coatings based on the siloxane block copolymer cured by gamma radiation preserved their protective properties for a longer time than heat- or chemically cured specimens. The possibility was thus established of using gamma radiation to produce organosilicon protective coatings for use in microelectronics. References: 11 Russian.

#### Strengthening Treatment of Polymer Material Parts

937M0018I Moscow PLASTICHESKIYE MASSY  
in Russian No 3, Mar 92 pp 40-41

[Article by A. A. Shturman and T. I. Reznichenko; UDC 678.744.322:539.4]

[Abstract] A study was made of the possibility of decreasing creep by hardening of polymer materials. Tests were performed on type AST-T plastic and SKhE-2 acrylate, heat treated in air with temperature rise rate 50° C/hr, cooling rate 0.2-0.6° C/min to 45° C, then 11-14° C/min to 20° C AST-T specimens were held 3 hours at 80° C, SKhE-2 specimens—1 hour at 110° C Creep was determined at a load of 20 MPa at 40° C. Relative compressive deformation under load was measured over a period of 50 s at various time intervals, 25 measurements in all. Relative compressive deformation decreased for both specimens, more significantly for AST-T. Hardening treatment was thus found to decrease the creep of both materials significantly. Figure 1; references 5 Russian.

#### Calculation of Crystallinity of Polar Polymers Based on Pyroelectric Currents Method

937M0018J Moscow PLASTICHESKIYE MASSY  
in Russian No 3, Mar 92 pp 42-43

[Article by N. N. Matveyev, V. V. Mordvinov, V. S. Voishchev, L. N. Nikitin and A. T. Bolgov; UDC 678.5.01:621.3]

[Abstract] A number of methods are known for determining the degree of crystallinity of polymer materials. This article

suggests a method of calculating this quantity based on measurement of pyroelectric currents upon crystallization of polar components. Polydimethyl siloxane (PDMS) was used as the model substance, as a typical crystallizing polymer. PDMS crystals have monoclinic syngony. The studies assumed that upon crystallization of PDMS with stretched chains, the only contribution to the change in polarization was that of the SiO bond, with the methyl side groups located so that the projection of their dipole moments on the Z axis was equal to zero. The number of crystals participating in formation of the pyroelectric phase was 1-2 percent. A density thermogram of pyroelectric current in crystallization of PDMS shows that the phase transition starts at 218 K, with the maximum at 199 K. An equation is presented for calculation of crystallinity based on these figures, and agrees well with experimental results from a previous work. Figure 1; references 7: 6 Russian, 1 Western.

### Fibers Based on Ceramic Forming Polymers

937M0037A Moscow KHIMICHESKIYE VOLOKNA  
in Russian No 3, Mar 92 pp 4-11

[Article by A. M. Tsirlin, G. A. Budnitskiy, Z. F. Yegorushkina, State Scientific Research Institute of Chemistry and Technology of Metal Organic Compounds, Moscow; All Union Scientific Research Institute of Fiber Production, Mytishchi; UDC 677.014 + 546.281.261]

[Abstract] Strong, highly modular, inorganic silicon carbide fibers may be obtained without a support by forming them from melts or metal organic polymer solutions followed by thermochemical treatment. A literature review was presented in this article covering their physical and chemical properties, structural characteristics and strength determinations. Then the reviewers discussed methods of preparation and modifications of principal products obtained. Several practical applications of these fibers were noted: in reinforcing ceramics, in production of components of rocket engines, in machinery construction, etc. Tables 3; figures 6; references 40: 9 Russian (1 by Western author), 31 Western.

### Intensification of Grafted Polymerization in Modification Process of Polycaprolamide Fibers

937M0037B Moscow KHIMICHESKIYE VOLOKNA  
in Russian No 3, Mar 92 pp 11-12

[Article by V. G. Zaikov, T. V. Druzhinina, L. S. Galbraykh, Moscow Textile Academy; UDC 677.494.675]

[Abstract] In spite of the fact that grafted copolymers of polycaprolamide and polydimethyl-aminoethyl-methylmethacrylate exhibit a series of interesting properties, their synthetic methods are quite ineffective or unnecessarily complex. Kinetics of this grafted polymerization initiated by oxidation-reduction systems (ORS):  $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$ - $\text{H}_2\text{O}_2$  and ORS containing a complex copper compound ( $\text{Cu}^{2+}$ - $\text{K}^+$ - $\text{H}_2\text{O}_2$ ) was investigated. It was shown that this reaction could be accelerated with the use of the last initiator: ORS- $\text{Cu}^{2+}$ - $\text{K}^+$ - $\text{H}_2\text{O}_2$ ; the yield of the grafted component was increased along with the more effective utilization of the monomer. Table 1; figures 2; references: 4 (Russian).

### Effect of Twisting on Composite Reinforcement of Complex Fibers From Rigid Chain Polymers

937M0037C Moscow KHIMICHESKIYE VOLOKNA  
in Russian No 3, Mar 92 pp 22-24

[Article by M. P. Nosov, N. I. Vagin, V. A. Smirnova, T. I. Kozhemyaka, V. I. Pirogov, Kiev Branch of All Union Scientific Research Institute of Fiber Production; UDC 677.017.33 + 539.383.2]

[Abstract] Twisting complex fibers produces consolidation of the ruptures of their component fibers; the same effect can be achieved by impregnation of the complex fibers with a binder. The effect of the impregnation of complex fibers with polyurethane carbazide coupled with twisting on their strength was investigated using domestically produced fibers ARMOS, SVM and Terlon. The experiment consisted of two phases: first the effect of the twisting alone was evaluated, then the combination of impregnation with twisting. Analysis of the data showed that combined effect of both measures resulted in significant strengthening of these fibers. This additional strengthening resulting from impregnation with a binder could be the result of a change in the rupture characteristic of elemental fibers changing from single towards multiple ruptures. The rupturing stress-twisting function  $\sigma(K)$  could be used effectively in evaluating composite strengthening of complex polymer fibers. Figure 1; references 14: 13 Russian, 1 Western.

### Production of Cord Fabric With Uniformly Dense Warp

937M0037D Moscow KHIMICHESKIYE VOLOKNA  
in Russian No 3, Mar 92 pp 27-28

[Article by V. N. Fedoseyev, V. A. Kuznetsov, V. P. Ivanov, All Union Scientific Research Institute of Fiber Production, Matishchi; UDC 677.4.061.43 + 677.054.845.2]

[Abstract] A new approach to the production of cord fabric with uniformly dense warp was reported. The authors used sectional reed on the weaving machine with varying teeth spacing; such a reed had a central zone with the smallest yet constant spacing and two outer zones symmetrically arranged on both sides of the center. Evaluation of such a weaving machine on the "Khimvolokno" plant in Svetlogorsk showed that the cord fabric produced exhibited uniform spacing of the fibers in the warp throughout its entire width. Table 1; figure 1; references: 3 (Russian).

### Plasma Treatment to Improve Adhesive Properties of Polymer Materials

937M0037E Moscow KHIMICHESKIYE VOLOKNA  
in Russian No 3, Mar 92 pp 31-32

[Article by I. N. Brovikova, V. L. Abramov, S. D. Menagarishvili, Ivanovo Chemical-Technological Institute; UDC 621.382:537.525]

[Abstract] One of the more promising methods of modifying polymer materials is based on treatment in low temperature gas discharge plasma. The plasma effect is limited to the surface layers only; the surface becomes hydrophilic and adhesive, making it possible to bind the polymer with various protective coatings. An attempt was made to produce metallized polyvinyl chloride films with adequate adhesive properties. In these experiments the use was made

of polyvinyl chloride films plasticized with dioctylphthalate and metallized with stainless steel powder. It was shown that, in order to obtain adequate binding of the metal to plastic, the latter must first be treated in oxygen plasma; similar results were actually also obtained in air plasma. A 5-10 min treatment gave a 3-5 fold increase in metal bonding to the polymer surface, even if the latter contained low molecular weight additives such as plasticizers. Tables 2; figure 1; references: 2 (Russian).

### Sorption Properties of Anion Exchange Fibrous Sorbents Based On Grafted Copolymers of Cellulose and Polyacrylonitrile

937M0037F Moscow KHIMICHESKIYE VOLOKNA  
in Russian, No 3, Mar 92 pp 34-37

[Article by L. V. Gulina, G. A. Gabriyelan, L. S. Galbraykh, N. I. Shcherbinina, G. R. Ishmiyarova, Moscow Textile Academy, Institute of Geochemistry and Analytical Chemistry, Moscow; UDC 677.494.675:677.027.622]

[Abstract] The goal of this work was to develop a method for production of modified grafted cellulose copolymers with polyacrylonitrile (PAN) based on the reaction of hydrazine hydrate with grafted PAN chains in presence of alkali metal hydroxides. Alkali metal hydroxides accelerate this reaction and lead to a more complete conversion of the nitrile group to hydrazide. The following order of the effect increase was noted: LiOH < NaOH < KOH. Overall, this reaction runs in two directions: a reaction of hydrazine with the nitrile groups to yield hydrazide, and formation of cyclic structures under the influence of OH<sup>-</sup>, resulting in formation of various byproducts. At the same time, increased concentration of KOH leads to an increased length of the conjugation chain. As a result, fibrous chemosorbents are obtained with excellent ion exchange capacity and satisfactory physical-mechanical properties. These sorbents were effective in extracting Ni, Cu, Zn, Cd, Pb, Y, Cr, Mn and Co from various solutions. Tables 3; figures 3; references 5: 2 Russian, 3 Western.

### Structural Characteristics and Properties of Composition and Ultra Fine Fibers From Mixed Polymer Melts

937M0037G Moscow KHIMICHESKIYE VOLOKNA  
in Russian No 3, Mar 92 pp 45-47

[Article by N. M. Rezanova, M. V. Tsebrenko, Kiev Technological Institute of Light Industry; UDC 677.494.014.578]

[Abstract] The structure and properties of fibers prepared from a mixture of polymer melts was studied; specific interactions among the components occurred in these melts at the phase separation borders depending on the conditions of melt deformation and on the properties of the starting polymers. Specifically, mixtures of ethylene polymer with vinyl acetate (EPVA) and co-polyamide (CPA) were used. The polymers were mixed either by extrusion or by suspension of a powder in benzene solution. The mixtures obtained by extrusion and containing 20, 30 or 40% of EPVA showed no fiber forming properties, probably because of an excessive hydrogen bond formation between the EPVA and CPA macromolecules. Overall, deformation

properties of ultra thin EPVA fibers resembled the properties of "Spandex"-type polyurethane fibers. Tables 4; figure 1; references: 5 (Russian).

### Recovery of Palladium From Solution of Pd, Au, Cu, Ag and Hg Dibutylthiophosphates

937M0116A Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 3-4, May-Jun 92 (manuscript received 10 Jul 91; in final form 13 Nov 91) pp 5-6

[Article by A.A. Zhuravlev, V.V. Rybnov and A.G. Ganiyev, Institute of Nuclear Physics, Uzbek Academy of Sciences; UDC 543.53]

[Abstract] A method has been developed for the recovery of Pd from a mixture of Pd, Au, Cu, Ag and Hg dibutylthiophosphates in nonane, using extraction with ammonium hydroxide. Two extraction with 10.00 M ammonium hydroxide led to 97-99% recovery of Au(I), Cu(II) and Ag(I), 17% Hg(II), abnd 0.2% Pd(II). Recovery of 50% of Hg(II) required 4 extractions with 6.5 M ammonium hydroxide. Recovery of Pd(II) required evaporation of the organic phase, and decomposition of dibutylthiophosphate with aqua regia to yield pure palladium chloride. References 3 (Russian).

### Catalytic Heterocyclization of Allyl Alcohol With Allylamine

937M0116B Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 3-4, May-Jun 92 (manuscript received 24 Oct 91; in final form 15 Feb 92) pp 49-51

[Article by S.M. Turabdzhyan, A.B. Kuchkarov and D. Yusupov, Tashkent State Technical University; UDC 547.361]

[Abstract] Heterocyclization of allyl alcohol with allylamine on a Zn/Cr/Al catalyst at 320-380° C resulted in the synthesis of a series of alky- and polyalkylpyrimidines. The respective rates of conversion of the alcohol and allylamine were 93.0 and 95.0%. Allyl alcohol undergoes dehydratation to propadiene and methylacetylene (1:1.5% by vol). Finally, reaction of allyl alcohol with ammonia leads to 3-methylpyridine, while cyclization of methylacetylene with allylamine results in the synthesis of 3,5-dimethyl-6-ethylpyridine and 2,3,4,6-tetramethylpyridine. References 6: 5 Russian, 1 Western.

### Polymerization and Copolymerization of N-Phenylacryloylbenzoxalone With Vinyl Chloride

937M0116C Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 3-4, May-Jun 92 (manuscript received 22 May 91; in final form 26 Nov 91) pp 54-56

[Article by B.L. Gafurov, S. Masharipov and M.M. Sulтанов, Institute of Polymer Chemistry and Physics, Uzbek Academy of Sciences; UDC 541.64.678]

[Abstract] Kinetic studies on radical polymerization of N-phenylacryloylbenzoxalone showed that the reaction proceeded with an energy of activation of 86.9 kJ/mole. The order of the process was 1.33 in N-phenylacryloylbenzoxalone and 0.60 vis-a-vis the initiator dinitrylazobisisobutyric acid. Analysis of copolymerization of N-phenylacryloylbenzoxalone with vinyl chloride yielded an

energy of activation of 156.77 kJ/mole. The order was 1.1 vis-a-vis the monomer and 0.61 in the initiator. Efficiency of polymerization was improved by inclusion of dichloroethane. Figures 3; references 6: Russian.

**Moderate Temperature Copolymerization of N-Vinylcaprolactam (NVC) With Acrylic Acid Initiated by Monomer-Initiator Systems**

937M0116E Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 3-4, May-Jun 92 (manuscript received 27 Feb 91; in final form 22 Sep 91) pp 71-74

[Article by M.S. Mirkhodzhayev, I.I. Ismailov and A.S. Rafikov, Tashkent Institute of Textile and Light Industry; Institute of Polymer Chemistry and Physics, Uzbek Academy of Sciences; UDC 541(64+128)]

[Abstract] Various spectroscopic and electrophysical techniques were used to demonstrate that reaction of NVC with the initiator dinitrylazo-bis-isobutyric acid resulted in complex formation, and that breakdown of the latter released radicals responsible for NVC polymerization. This phenomenon was also found to underlie low-temperature radical copolymerization of NVC with acrylic acid. The minimal temperatures for copolymerization in DMSO (with dielectric constant,  $\epsilon$ , of 45.0), DMF ( $\epsilon$  = 36.7) and ethanol ( $\epsilon$  = 24.3) were 287, 290 and 293, respectively. Accordingly,

solvents with high  $\epsilon$  values favor breakdown of the monomer-initiator complexes to radicals and, consequently, facilitate low-temperature radical copolymerization of NVC with acrylic acid. Figures 3; references 4: 3 Russian, 1 Western.

**Mass Balance and Thermodynamics of Isopropanol Conversion to Acetone on Ag/Aluminosilicate Catalyst**

937M0116F Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 3-4, May-Jun 92 (manuscript received 24 Jul 91; in final form 10 Sep 91) pp 78-81

[Article by R. Kh. Karimov and M.M. Azizov, All-Union Scientific Research Institute of the Medical Industry; UDC 661.727:547.284]

[Abstract] Mass balance analysis of isopropanol conversion to acetone on an Ag/aluminosilicate catalyst (D-53) revealed that at equilibrium an input of 0.860 moles of reactants (incl. 0.187 moles of isopropanol) was balanced by 1.000 moles of products (incl. 0.180 moles of acetone). Thermodynamic calculations further demonstrated that over a 400-800 K range heat consumption (4734.8 cal/mole) was essentially balanced by output (4679 cal/mole), with the reactive gas mixture at ca. 800 K (527° C) at the end of the process. Since gas temperature at the upper reaches of the gas layer is ca. 150° C, the sharp temperature drop between the catalyst and gas indicates that under these conditions—which are analogous to commercial processes—production of acetone is diffusion dependent. References 6: Russian.

## RADIATION CHEMISTRY

### Mean Specific Energy Absorbtion in Track Core as Possible Equivalence Parameter of Radiation of Various Ions

927M0228A Moscow KHIMIYA VYSOKIKH ENERGIY in Russian Vol 26, No 1, Jan-Feb 92 (manuscript received 23 Feb 90) pp 20-26

[Article by A. M. Mitrev, D. Yu. Mamedyarov, and I. G. Kaplan, Physical Chemistry SRI imeni L. Ya. Karpov, Moscow; UDC 541.15]

[Abstract] This work was carried out in accordance with contract No 5292/B of the International Agency on Atomic Energy. Other conditions being equal, radiation effects are determined not only by the magnitude of the dose, but also by the type of radiation. This is especially clear in the case of irradiation of condensed media with various types of ions. The reason for this effect lies in the differences in energy variations within the charged particle tracks. The shape of an ion track depends on several parameters of the ion, and as a result attempts to use a single universal parameter to adequately describe track size and density variations of primary active particles within it, disregarding ion type, proved unsuccessful. The inadequacy of linear energy loss as such a parameter is due to the single dimension feature of this characteristic, since radiational changes occur within the bulk, i.e. they are a function of the concentration of primary activations formed in the tracks as a result of ionic activity. Furthermore, for practical purposes in the problem of equivalence of radiational activity (while simulating or predicting effects, for example), it is useful to have such a characteristic of radiation (or equivalence parameter) which could be used to at least approximately evaluate the tendency for change in effect resulting from the substitution of one type of radiation for another. In the present work methodology and results are presented on computing the mean specific energy absorption within the track core of a heavy ion ( $D_c$ ). Differential yields of  $Fe^{3+}$  ions, obtained during radiolysis with various ions, are compared with values for  $D_c$ . The characteristics of track  $D_c$  is proposed for use as an initial value in constructing an equivalence parameter. Figures 2; references 14: 5 Russian, 9 Western.

### Intermediade Radiolytic Conversion Products of 6-Aminophenalenone in Ethanol

927M0228B Moscow KHIMIYA VYSOKIKH ENERGIY in Russian Vol 26 No 1, Jan-Feb 92 (manuscript received 5 Apr 91) pp 33-39

[Article by G. V. Semenova, A. V. Ponomarev, L. I. Kartseva, and A. K. Pikayev, Physical Chemistry Institute, Moscow; UDC 541.15]

[Abstract] Impulse radiolysis was used in a previous work to study radiolytic conversion with semi-reduced 6-aminophenalenone in aqueous solutions. It was proposed that both the anion radicals ( $Kp^-$ ) and the H-adducts ( $KpH$ ) of the dye could have two different structures, viz. one with the excess electron localized at one of the carbon atoms of the phenalenone ring, and another where it is localized at the carbonyl group. It is possible that similar phenomena could also be observed during radiolysis of alcoholic solutions of 6-aminophenalenone. A study was made in the present work of the above processes in ethanol under

various conditions. In alkaline media the basic products are anion-radicals of 6-aminophenalenone with absorption bands at 355 and 400 nm. In neutral and acid media, the anion-radical becomes protonized in reactions with alcohol and hydrogen ions. The resulting H-adduct of 6-aminophenalenone has absorption maxima at 350 and 390 nm. Evidently, the presence of the two maxima is related to the two different structures of the product. Estimates were made of the molar extinction coefficients of the H-adduct of the 6-aminophenalenone and the reaction rate constants with their participation. Figures 4; references 6: 5 Russian, 1 Western.

### Radiation Copolymerization of N-Vinylpyrrolidone with Diethylaminoethylmethacrylate and Its Quaternary Ammonium Salt

927M0228C Moscow KHIMIYA VYSOKIKH ENERGIY in Russian Vol 26 No 1, Jan-Feb 92 (manuscript received 15 Jun 90) pp 45-48

[Article by V. N. Ushakova, N. A. Afanakina, Ye. F. Panarin, and V. M. Denisov, High Molecular Compounds Institute; UDC 541.15:66.096.268:678.746.527-547.91.3]

[Abstract] Water soluble copolymers of N-vinylpyrrolidone with aminoacrylates and their quaternary ammonium salts display various types of biological activity and are used as carriers for biologically active substances. The goal of the present work was to study the copolymerization of N-vinylpyrrolidone with 2-(N,N-diethylamino)ethylmethacrylate and its quaternary ammonium salt in aqueous solution using  $\gamma$ -radiation. Water soluble polymers were prepared which appear promising as possible modifiers for biologically active substances. Figures 2; references 6: 5 Russian, 1 Western.

### Hydroxyl Compounds of Pentavalent Plutonium

927M0237A St. Petersburg RADIOKHIMIYA in Russian Vol 34 No 2, Mar-Apr 92 (manuscript received 27 May 91) pp 1-4

[Article by I. G. Tananayev; UDC 546.799.4.5]

[Abstract] Crystalline hydroxides of neptunium and americium have been prepared previously in alkaline media. In the present work crystalline pentavalent plutonium hydroxides were similarly prepared by reduction of hexavalent plutonium in formaldehyde or potassium iodide in LiOH, KOH, and RbOH solutions in alkali concentrations of not less than 4 moles per liter. Preparation of these compounds serves as the first confirming proof of the existence of plutonium (V) in alkaline media as a hydrocomplex. References 10: 6 Russian, 4 Western.

### Electron Structures of Tetrachlorides of Zirconium, Hafnium, and Kurchatovium

927M0237B St. Petersburg RADIOKHIMIYA in Russian Vol 34 No 2, Mar-Apr 92 (manuscript received 17 Jul 91) pp 4-10

[Article by M. V. Ryzhkov and V. A. Gubanov; UDC 539.194:546.79]

[Abstract] One of the problems of the influence of the relativistic effect on the chemical characteristics of the

transuranium elements concerns the possibility of stabilizing the p- orbitals of atoms at the end of the 5f- and beginning of the 6d- series of the periodic system. It has often been proposed that the 7p- shell is complete in elements of the 6d- type. However, these conclusions were made chiefly for the basic state of isolated atoms, while the situation in compounds is more complex. Many experiments on determining the characteristics of kurchatovium indicated that they are similar to the parameters of Zr and Hf molecules and differ from compounds of the elements of the IVb subgroup. Theoretical simulation of the electron structure of molecules containing Ku were either carried out in non-relativistic approximations, or in a single centered decomposition suitable only for hydrates. In the present work a relativistic method of discreet variation was used to compute the electron structures of the title compounds. On the basis of data on the energies and structures of molecular orbitals, it was concluded that the electron structures of the three compounds are similar. As the element number increases, so do the s- and in some cases the p- orbitals. References 18: 3 Russian, 15 Western.

#### Redox Reactions of Platinum Elements. Part VIII. Rhodium (IV) Hydrogen Peroxide Reaction Kinetics

927M0237C St. Petersburg RADIOKHIMIYA in Russian  
Vol 34 No 2, Mar-Apr 92 (manuscript received 7 May 91)  
pp 35-41

[Article by V. S. Koltunov and A. B. Khaperskaya; UDC 546.97:541.17]

[Abstract] The kinetics of certain redox reactions of ruthenium and platinum were studied previously and the present work is devoted to rhodium. While the literature contains references to the instability of rhodium compounds in oxidation states exceeding +3, the authors' research shows that rhodium (IV) is sufficiently stable in both perchloric and nitric acids and only slowly converts to the trivalent state. The redox reactions of rhodium, particularly the oxidation of Rh(III) and the reduction of Rh(IV), become especially interesting from a practical standpoint in developing a plan for leaching this element out of spent nuclear fuel cells. According to IAEA data, the rhodium content in the irradiated uranium of a water-cooled nuclear reactor is 0.45 kg per ton, and extraction is a profitable venture. The reaction rate constant for the reduction of tetravalent rhodium with hydrogen peroxide in perchloric acid is independent of the hydrogen ion concentration and the ionic strength of the solution. Activation energy, entropy of activation, as well as the reaction rate constant were determined and the mechanism of the reaction discussed. Figures 2; references 8: 7 Russian, 1 Western.

#### Extraction of Trivalent Transplutonium Elements with High Molecular Amines from Acid Solutions

927M0237D St. Petersburg RADIOKHIMIYA in Russian  
Vol 34 No 2, Mar-Apr 92 (manuscript received 1 Apr 91)  
pp 57-65

[Article by M. S. Milyukova, Ye. V. Kuzovkina, D. A. Malikov, and B. F. Myasoyedov; UDC 542.61]

[Abstract] Extraction of trivalent transplutonium elements with high molecular aliphatic amines from mineral acid solutions is almost impossible. They can be readily extracted from concentrated solutions of lithium chloride or nitrate and low acid content. In the present work results are presented on the extraction of trivalent transplutonium elements with high molecular amines from mineral acid solutions containing "unsaturated" heteropoly compounds of the 17th and 11th series in insignificant concentrations ( $10^{-4}$  -  $10^{-3}$  mole per liter). Primary and secondary amines are capable of extracting the above elements from sufficiently concentrated solutions of mineral acids almost quantitatively. Tertiary alkyl amines can extract 80-90 percent from moderately concentrated (0.05 - 0.1 mole per liter) acid solutions. The elements may be extracted at over 65 percent from 0.1 mole per liter hydrochloric acid solutions with quaternary ammonium bases. Figures 7; references 14: 7 Russian, 7 Western.

#### Study of Extraction and IR-Spectra of Complexes of Transplutonium and Rare Earth Elements with Phosphorylated Methypyridines and Their N-Oxides

927M0237E St. Petersburg RADIOKHIMIYA in Russian  
Vol 34 No 2, Mar-Apr 92 (manuscript received 22 Sep 90)  
pp 65-72

[Article by G. V. Bodrin, L. A. Ivanova, Ye. I. Matrosov, M. K. Polikarpov, B. F. Myasoyedov, and M. I. Kabachnik; UDC 542.61:(546.791+546.799+546.661)]

[Abstract] Certain neutral bidentate organophosphorus reagents, such as tetraarylmethyldiphosphine dioxides or diaryl[dialkylcarbaminoylmethyl]phosphine oxides, are effective in extracting transplutonium and rare earth elements and may be used for group concentrating purposes during extraction from nitric, perchloric, or phosphoro acid solutions. Attempts to separate transplutonium and rare earth elements by using this type of reagent showed that they are not selective enough. Other work demonstrated that the separation may be improved by using N- and S-donor reagents. In the present work a study was made of the extraction capability and selectivity of some neutral organophosphorus reagents containing two P-O-groups and a pyridine nitrogen. Diphosphoryl compounds had separation factors of 4-5 as compared to 1.0 for tetraphenylmethylenediphosphine dioxide in regard to extraction of americium (III) and europium (III). Neodymium (III) complexes were introduced and analyzed. IR-spectra showed that phosphorylated methypyridine behaves as a bidentate in complex formation. Coordinated with a metal, only two P-O-groups participate, while the N-oxide behaves as a tridentate reagent where the N-O-group participates as well as the two P-O-groups in coordination with a metal. Figures 4; references 12: 6 Russian, 6 Western.

**Thin Layer Chromatography of Strontium and Yttrium Isotopes**

927M0237F St. Petersburg RADIOKHIMIYA in Russian  
Vol 34 No 2, Mar-Apr 92 (manuscript received 18 Apr 91)  
pp 88-95

[Article by V. A. Ryabukhin, M. P. Volynets, and B. F. Myasoyedov; UDC 541.183]

[Abstract] The growing interest in studying the behavior of artificial radio nucleides in the environment and predicting their effects on humans has stimulated further improvements in the methods of determining radioisotopes, particularly Sr<sup>89</sup> and Sr<sup>90</sup>, in soils, water, and biological and other matter. Conventional methods start by separation of radiostrontium from other radioactive and non-radioactive elements. Known methods of strontium precipitation employing hydroxide, oxalate, sulfate, and chromate ions and other reagents have many disadvantages such as numerous precipitation, filtration, and drying operations. Columnar chromatography is time consuming owing to the large volumes of eluents and special stages of preparing counting grids. Extraction separation of strontium employing selective extractants, particularly crown-esters, is apparently the most modern method. In the present work a study was made of the behavior of radioactive strontium, yttrium, and other satellite radioactive isotopes on thin plates by thin layer chromatography in conjunction with the development of an extraction-chromatographic method for separating radiostrontium in soil samples. By using a variety of organic solvents as eluents, conditions were found for cleansing the radiostrontium from excess extractant and radioactive impurities, as well as daughter Y<sup>90</sup>. A thin layer chromatographic technique is proposed that is supplemental to known methods of selective separation of strontium from soil samples using crown-ester. Figure 1; references 8: 4 Russian, 4 Western.

**Preparation and Properties of Glass Composite Materials for Hardening Radioactive Wastes**

927M0237H St. Petersburg RADIOKHIMIYA in Russian  
Vol 34 No 2, Mar-Apr 92 (manuscript received 16 Apr 90)  
pp 143-148

[Article by M. I. Ozhovan and O. K. Karlina; UDC 666.1:621.039:763]

[Abstract] In treating radioactive wastes by glassification, difficulties associated with phase separation are frequently encountered whereby individual waste components (molybdates, sulfates, chlorides) form a water-soluble phase not miscible with borosilicate glass and containing radio nucleides which tend to lower the water solubility of the end product and the radioactive safety of the waste material. Separation of this phase also causes other technological problems in the glassification process such as increasing the volatility of radio nucleides and components of the immiscible phase, increased energy consumption in the glassification process, and refractory corrosion in the glassification furnace. Components not compatible with borosilicate glass could be included in this glass when used to make glass composite materials. In the present work a study was made of the possibility of preparing a glass composite material in which the matrix is a stable borosilicate glass containing insoluble components, mainly radioactive sulfate wastes, as a dispersed phase. The sulfate wastes were dispersed mechanically in the glass melt and cooled. The composites were then tested for resistance to sodium and sulfate ion leaching with water. Deliberate destruction of the composite samples during testing for water resistance did not result in increased component leach rate. Figures 4; references 7: 2 Russian, 5 Western.

**Robotized Synthesis of [<sup>18</sup>F]-2-Fluoro-2-Desoxy-D- Glucose**

927M0237G St. Petersburg RADIOKHIMIYA in Russian  
Vol 34 No 2, Mar-Apr 92 (manuscript received 27 May 91)  
pp 129-135

[Article by M. Yu. Kiselev, D. V. Solovyev, and M. V. Korsakov; UDC 621.039.554:616-073.916]

[Abstract] The synthesis of the title compound (FDG) is one of the fundamental tasks of radiochemical laboratories engaged in the synthesis of radiopharmaceuticals designated for human diagnostic methods using positron emission tomography (PET). Research is now initiated at the Brain Institute, Moscow on glucose metabolism in the brain using FDG administered parenterally. Currently, a program has been developed for providing tagged preparations for PET diagnostics, including the development of FDG synthesis. FDG synthesis in many foreign countries has become routine. The second of two general methods for the synthesis is based on a nucleophilic method developed by K. Hamacher employing [<sup>18</sup>F]F<sup>-</sup> generated in the target of a cyclotron filled with water enriched with O<sup>18</sup> by the reaction <sup>18</sup>O(p, n)<sup>18</sup>F. In the present work FDG was synthesized by robot from the cyclotron-generated [<sup>18</sup>F] fluoride by the Hamacher method. The teteracetyl derivative of FDG, an intermediate, was purged from the product which was also free of catalyst impurities. Radiochemical purity of the end product was not less than 95 percent and the radiochemical yield was 20-30 percent. Figure 1; references 13 (Western).

**The Metal Content of the Ore-Forming Fluids of the Gold-Silver-Polymetal Deposits of the Banska-Shtyavnitsa Deposit in Central Slovakia**

937M0004A Moscow DOKLADY AKADEMII NAUK  
in Russian Vol 324 No 2, May 92 (manuscript received  
19 Feb 92) pp 425-429

[Article by V.Yu. Prokofyev, F.G. Reyf, Yu.M. Ishkov, and V.A. Kovalenker, Geochemistry Institute imeni A.P. Vinogradov, Siberian Department, Russian Academy of Sciences, Irkutsk, Buryat Geological Institute, Siberian Department, Russian Academy of Sciences, Ulan-Ude, and Institute of Ore Deposit Geology, Petrography, Mineralogy, and Geochemistry, Academy of Sciences, Moscow; UDC 553.2:550.246]

[Abstract] The Banska-Shtyavnitsa epithermal gold-silver-polymetal deposit in Central Slovakia was studied in detail as a characteristic representative of a deposit rich in ore-forming fluid inclusions. The Banska-Shtyavnitsa deposit was formed from a series of long (3 to 7 km) sulfide-carbonate-quartz veins lying in propylitized andesites, dacites, and diorites in zones of endo- and exocontacts of the intrusive mass of the granodiorites of the Shtyavnitsk-Godrushsk complex. The ore deposit is between 11 and 16 million years old. The process of mineral formation in the deposit was found to have proceeded in five stages, primarily by the formation of open cracks and intensive intramineralization tectonics. Samples of fluid inclusions from the deposits were subjected to thermo- and cryometric and laser-spectral studies that indicated that the formation of commercial mineralization in the Banska-Shtyavnitsa deposit was the result of the presence of solutions rich in ore elements. The composition of the ores in the various veins is

also dictated by high concentrations of profiling metals in the thermal springs that formed the veins. By themselves, the chloride complexes found were insufficient to account for the high concentrations of metals discovered. Fluoride and sulfate complexes had to be involved in the ore formation process as well. The data obtained from the analyses of the fluid inclusions reflected two different processes: a process of ore sedimentation from thermal springs that acted as reducing agents and a process of resedimentation of the ores in circumstances conducive to oxidation. Figure 1, table 1; references 13: 10 Russian, 3 Western.

**The Behavior of Cu, Ag, Pt, Pd, and Au in the Process of the Crystallization of Stratified Kivakksk Intrusive Rock (Northern Karelia)**

937M0006A Moscow DOKLADY AKADEMII NAUK  
in Russian Vol 323 No 5, Apr 92 (manuscript received  
28 Jan 92) pp 935-938

[Article by N.F. Pchelintseva and Ye.V. Koptev-Dvornikov, Moscow State University imeni M.V. Lomonosov; UDC 550.42]

[Abstract] Kivakksk differentiated intrusive rock, which cuts through the metamorphic rock of the Upper Archean, is located in the Baltic shield. The instructive rock contains olivinite, norite, gabbronorite, and gabbroic zones and is about 2 km thick at its center. The behavior of Cu, Ag, Pt, Pd, and Au in the intrusive rock was studied by the atomic absorption method on a Hitachi model 207 atomic absorption chromatograph. The mean-weighted amounts of the said elements in the intrusive rock were determined to be as follows: Cu, 85.2 g/t; Ag, 37.7 mg/t; Au, 2.18 mg/t; Pd, 22.2 mg/t; and Pt, 7.3 mg/t. The behavior of the study ore elements during the process of the intrusive rock's solidification was hypothesized to be controlled by fractionation of the sulfide phase. Higher values of the coefficients of destruction between the sulfide phase and silicate melt were obtained for Pt, Pd, and Au than for Cu and Ag. Sulfide-phase fractionation of the noble metals was more effective than was sulfide-phase fractionation of the Cu and Ag; consequently, they were concentrated in the low-sulfide horizons of the layers of rock of the third (predominately norites and bronzites) and fourth (predominately norites) megarythms, thus resulting in a regular increase in the values of the ratios of Cu and Ag to Pt, Pd, and Au in the gabbronorites and gabbroic zones of the upper portion of the intrusive rock. Figures 2, tables 2; references 9: 5 Russian, 4 Western.

**The Forms of Gold in the Ores of Deposits Classified as Carbon-Containing Rock**

937M0006B Moscow DOKLADY AKADEMII NAUK  
in Russian Vol 323 No 5, Apr 92 (manuscript received  
6 Feb 92) pp 939-941

[Article by N.I. Razenkova, B.S. Kogan, Ye.N. Sharopova, and T.V. Filippova, Mineralogy, Geochemistry, and Crystal Chemistry of Rare Elements Institute, Moscow; UDC 550.42:546.59]

[Abstract] An experimental study was conducted to determine the forms in which gold is present in deposits classified as gold-pyrite-arsenopyrite formations. The deposit site studied consisted of intensively dislocated shales with lenses

of marbelized limestones. The rhythmically layered blocks of lithofacies studied contained quartz-mica, quartz-calcite-mica, quartz-graphite, graphite, and carbonate shales characterized by a gradual change in the ratios of the carbon and carbonate materials contained in them. The main primary mineral ores in the ore-enclosing formations studied were pyrite, pyrrhotine, arsenopyrite, antimonite, scheelite, chalcopyrite, and gold nuggets, and more rarely, sphalerite, galenite, and cinnabar. Gold was found to be a "through" element of all products of the hydrothermal-metasomatic stage. The highest concentrations of gold were found in narrow zones of the development of quartz-mica metasomatites and graphitic quartzites rich in arsenopyrite of all subsequent generations. The method of phase chemical analysis involving the use of solutions of hydrochloric acid and nitrohydrochloric acid was used to study the forms in which gold was present in partially oxidized ores. In the five ore samples and series of ore filtrates studied, gold was determined (by the atomic absorption method) to be present in amounts ranging from 4.8 to 8.1 g/t. The studies established that in partially oxidized ores, gold may be present in sulfides, quartz, or the carbon matter of enclosing rock, as well as in loose supergene formations. Its appearance in diluted hydrochloric acid solutions can only be explained in terms of the dissolution of finely dispersed gold from minerals with a loose matrix (such as limonite, goethite, etc.). Gold in this particular form was found in all of the samples examined and was at a maximum in the two samples that were rich in ore matter. Sulfide gold dissolved in nitrohydrochloric acid was only found in the latter two samples, where it reached a concentration of 60 rel.-%. A third form of gold, i.e., inextractable gold bound to some sort of minerals that remained inert to the solvents used, was also present in all of the samples studied. In some cases, it constituted practically 100% of the total metal content. Table 1; references 5 (Russian).

### The Genesis of Curved-Facet Timan and Ural Diamonds

937M0007A Moscow DOKLADY AKADEMII NAUK  
in Russian Vol 323 No 4, Apr 92 (manuscript received  
7 Feb 92) pp 752-755

[Article by B.A. Malkov, Ukhta Industrial Institute; UDC 549.211(234.83+234.85)]

[Abstract] The genesis of curved-facet "Ural"-type diamonds, which are prevalent in the Timan and Ural placer deposits, northeastern Yakutia, Namibia, the kimberlites of the province of Northern Russian, and the Republic of South Africa among other places, has long been a puzzle. Various researchers have proved that curved-facet diamonds of the Ural type are the end forms of the dissolution of flat-facet crystals. The exact nature of the process and the agents facilitating it have remained unclear, however. Although the idea of the oxidative dissolution and corrosion of diamonds by kimberlite magma seems preferable at first glance, there have been observed cases of curved-facet crystals regenerating and transforming into flat-faceted octahedra that could later have been subjected to rounding. There have also been rare instances of flat- and curved-facet diamonds being present together in xenoliths of mantle eclogites of various pipes. The combination curved- and flat-faceted crystals in these xenoliths are nitrogen-free, and all octahedral crystals have nitrogen-free nuclei and a

periphery containing nitrogen in different forms. The round surfaces of these combination curved- and flat-faceted crystals intersecting the grown zones are secondary, which is to say that they form in a "dissolution" process. The explicit locality of this dissolution suggests that it occurred in a solid rock matrix whose density and degree of cracking depends on the action of corrosive agents on the crystal. The evidence suggests that the observed instances of the "regeneration" of flat facets occurs as follows. The curved-facet diamonds of the early stage are formed while the diamond phase is relatively stable with episodic increases in its oxidation potential leading to the "dissolution" of flat-faceted octahedra. After conditions normalize, the dissolved octahedral zones are regenerated, and flat-faceted octahedra form. Curved-facet diamonds of the late stage, on the other hand, form in a range that is already metastable for diamond, when the oxidation potential of the medium is irreversibly elevated and the regeneration process becomes fundamentally impossible. The rounding of crystals of the late stage is evidently not related to the process of the generation of kimberlite magma that subsequently transports the diamonds to the surface but rather depends, first and foremost, on the unique oxidation conditions characteristic of the diamond-bearing lithosphere of entire provinces. The diamond-bearing Ural and Timan ridges date from the Devonian period. The characteristic curved-facet habit of the diamonds in the Timan and Ural paleoridges is analogous to the habit of the diamonds of the Northern Russian Middle Paleozoic kimberlite province, where only kimberlites of the Late Devonian-Early Carboniferous period are known to date. The evidence suggests that on the Russian platform in the Paleozoic period there existed other more ancient pre-Devonian kimberlites that were fed with curved-facet diamonds of the paleoridge of the early and middle Devonian periods at the site of the currently existing structures of the Western Urals and the Timan Ridge. References 15: 11 Russian, 4 Western.

### The Solubility of Gold at 500 and 600° C ( $P_{tot} = 1$ kbar) in the Presence of Iron Oxides and Sulfides

937M0008A Moscow DOKLADY AKADEMII NAUK  
in Russian Vol 323 No 2, Mar 92 (manuscript received  
15 Jan 92) pp 294-298

[Article by G.G. Likhoydov, corresponding member, Russian Academy of Sciences, and I.Ya. Nekrasov, Far Eastern Geology Institute, Far Eastern Department, Russian Academy of Sciences, Vladivostok; UDC 550.8.014:546.57]

[Abstract] A series of experiments was conducted to estimate the solubility of gold in the presence of a hematite-pyrite-magnetite buffer at 500 and 600° C under a total pressure of 1 kbar. A concentration of 0.1 M HCl was used in most of the experiments conducted. The starting sample thus contained magnetite, hematite, elemental sulfur, and a pyrite inoculant. The sulfur and hematite used were graded chemically pure. The synthetic magnetite used was synthesized at 600° C under 1 kbar pressure over the course of 48 hours. Bidistilled waters and HCl and  $H_2SO_4$  solutions were also used. The experiments were performed in gold ampules measuring 8 mm in diameter and up to 70 mm in length (the metal was 99.99% pure). The ampule walls served as a gold source for the solutions. The amount of solution used in the experiments ranged from 1 to 1.5 ml. Each experiment lasted from 3 to 5 minutes, with the pressure increased

throughout. The ampules' leaktightness was controlled by weighing. Hydrothermal units with a temperature precision of +/- 5° and a pressure precision of +/- 50 bar was used. At 500° C, the content of gold in the solutions after the conclusion of the experiments ranged from 2.59 to 10.0 x 10<sup>-6</sup> M, thus averaging 6.3 x 10<sup>-6</sup> or 1.2 g/t gold. This was somewhat lower than the solubility measured for the very same temperature and pressure conditions in 1 M NaCl (1.5 g/t) (as reported elsewhere) and 1.5 to 2 orders of magnitude higher than the concentration of gold in water (0.02 to 0.09 g/t). When the experiments were repeated under identical conditions but at a temperature of 600° C, the field of hematite thinned out in the presence of sulfides. Even in the first hours of exposure, the hematite of the starting sample, even when taken without magnetite, was completely replaced by the latter, and the appearance of pyrite made it necessary to increase the starting amount of sulfide approximately twofold as compared with conditions at 500° C. The solubility of gold at 600° C fluctuated from 0.63 to 5.01 x 10<sup>-6</sup> M (0.13 to 0.99 g/t), averaging 1.19 x 10<sup>-6</sup> M gold (0.23 g/t). Despite the fact that the intervals of the solubility values measured for gold at 500 and 600° C partially overlapped, the researchers concluded that as the temperatures between the two points increased, the concentration of gold in the study solutions decreased severalfold within the confines of one and the same order of magnitude. This was attributed to the special features of complexing where the domination of sulfate forms in the solutions inhibits the sulfide forms that dictate the solubility of gold under these conditions. Figure 1, table 1; references 10: 5 Russian, 5 Western.

#### Local Laser Electrodeposition of Gold on Copper Cathodes of Rectangular, Cylindrical and Spherical Shapes

937M0038D Moscow ELEKTROKHIMIYA in Russian  
Vol 28 No 5, May 92 (manuscript received 1 Apr 91)  
pp 730-735

[Article by Yu. V. Seryanov, L. V. Aravina; UDC 669.248:539]

[Abstract] Wide use of local galvanic precipitation of gold in radio-electronic industry resulted in an increased interest in the economy of such processes. One of the most promising methods is based on local laser heating of the metal-electrolyte border. A semi-empirical method of solving some practical problems was published previously for calculating local temperature field of laser heating, based on the analysis of the kinetic data of "heat expansion" of local metal precipitate. This approach was applied to cathodes with typical dimensions exceeding substantially the length of the heat wave. A mathematical expression was developed relating the temperature of local heating of the cathode surface with a focused laser beam to the radius of a spot of local metal precipitate, which could be called a "quasi-regulatory" temperature field equation. This equation was used effectively in laser-electrochemical precipitation of

gold to form designs on curved metallic dielectrics or semiconductors. Table 1; figures 4; references 9: 7 Russian, 2 Western.

#### Comparison of Electrochemical Properties of Metallurgic Silver and Electroplated Silver Coatings by Estance Method

937M0038G Moscow ELEKTROKHIMIYA in Russian  
Vol 28 No 5, May 92 (manuscript received 5 Jul 90)  
pp 806-809

[Article by G. V. Valinchus, Vilnius University; UDC 541.135.5]

[Abstract] Experimental results were reported of the determination of estance of silver coatings precipitated from cyanide, dicyano-silver thiocyanate and iodide electrolytes. Analysis of the results showed that Ag-coatings from cyanide solutions containing small quantities of KCN, at sufficiently negative potentials are resembling quite closely metallic silver by their electrochemical properties. On the other hand, silver coatings from iodide electrolytes differ markedly from metallic silver, probably because of surface contamination with iodine. Furthermore, Ag-surfaces electroplated from electrolytes with high content of CN<sup>-</sup> or SCN<sup>-</sup> are contaminated and their properties are difficult to reproduce. The estance method "sees" the differences at the level of surface atomic layers, hence it could be used effectively in diagnosis of the properties of electroplated metals in galvanic technology. Figures 3; references 6: 4 Russian, 2 Western.

#### Geological-Geochemical Model of Gold Deposit Formation in Ophiolitic Belts

937M0041A Moscow GEOKHIMIYA in Russian  
No 2, Feb 92 (manuscript received 6 Mar 90) pp 178-188

[Article by A. F. Koroveynikov, Tomsk Polytechnical Institute; UDC 550.42]

[Abstract] The authors have developed a theory to explain the formation of major ore fields which develop in or around the ophiolitic belts of carbonaceous shales. The theory was used in a systematic study of the distribution of gold in the ophiolitic belts of the Urals, east Kazakhstan, Kuznetskiy Alatau, west Sayan, and East Tuv. Data on the zonal distribution of various elements, isotopes, and ores was reviewed. Neutron activation and polarography were used to measure the gold content of basite-hyperbasite, granitoid, and metasomatic formations in the regions studied. The distributions observed confirm that gold deposit formation occurred during autometasomatism and hydrothermal metasomatism caused by basite-hyperbasite ophiolite belt intrusions. These processes resulted in gold splitting off from basite-hyperbasite rocks and saturating ore-forming hydrotherms. About 20%-40% of the gold was removed and redistributed by early alkaline hydrotherms, so that it accumulated in sulfide-bearing listwanite-beresites and metasomatic zones. Greenstone metamorphism of the magmatites did not substantially alter gold redistribution and accumulation. Figures 2; references 21: Russian.

## MISCELLANEOUS

JPRS-UCH-93-002  
28 January 1993**On Finding Liquified Gas in Natural Diamond**

937M0041B Moscow GEOKHIMIYA in Russian  
No 2, Feb 92 (manuscript received 1 Jan 91) pp 268-273

[Article by D. K. Voznyak, V. N. Kvasnitsa, and T. Ya. Kislyakova, Institute of Geochemistry and Mineral Physics, Ukrainian Academy of Sciences, Kiev; UDC 548.4+549.211]

[Abstract] A cryometric method was used to reveal the presence of liquid inclusions in one of 44 Bilyakh River Yakutiya diamond samples. The closeness of the inclusion melting temperature, -66.8° C and the CO<sub>2</sub> triple point, indicated that the inclusion is partly CO<sub>2</sub>. Data from previous works suggests that the remainder is most likely nitrogen. The ratio of nitrogen to carbon dioxide was estimated to be about 5:1. The findings are in agreement with results obtained by other investigators using heat and/or vacuum to study evolution of volatile components from Yakutiya diamonds. The data indicate that the study of fluid inclusions can assist in the solution of questions as to the origin of diamonds and conditions of surface mantle formation. Figures 2; references 24: 18 Russian, 6 Western.

**Diamonds in Carbonaceous Chondrite Yefremovka CV3**

937M0042A Moscow GEOKHIMIYA in Russian  
No 1, Jan 92 (manuscript received 02 Nov 90) pp 155-159

[Article by A.V. Fisenko, L.F. Semenova, V.F. Tatsiy, G.V. Baryshnikova and A.K. Lavrukhina, Institute of Geochemistry and Analytical Chemistry imeni V.I. Vernadskiy, USSR Academy of Sciences, Moscow; UDC 552.63:549.211]

[Abstract] X-ray spectroscopy and differential thermography were used in an analysis of meteoric diamonds—characterized by an anomalous Xe-HL component—found in carbonaceous chondrite CV3. The resultant observations were compared with data derived for natural and synthetic diamonds. The meteoric diamond fraction—ca. 0.02% of the chondrite by weight—was represented by single crystals with similar dimensions and susceptible to thermooxidative graphitization. Synthesis of these diamonds under nonequilibrium conditions was accompanied by significant replacement of carbon atoms by nitrogen atoms to an extent not evident in natural diamonds. Formation of the meteoric diamonds evidently occurred under the impact of shock waves on gaseous carbon atoms in the initial stages of helium combustion in the convective nucleus. Figures 1; tables 1; references 18: 8 Russian, 10 Western.

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